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Groundwater salinity and hydrochemical processes in the volcano-sedimentary aquifer of La Aldea, Gran Canaria, Canary Islands, Spain

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HIGHLIGHTS

- High groundwater salinity results from aridity.
- Return irrigation flows are an important recharge source.
- Groundwater reserves are essential in dry periods.
- Groundwater quality is poor and needs mixing or desalination.
- An exception to the European Water Framework Directive is needed.

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ABSTRACT

The origin of the groundwater salinity and hydrochemical conditions of a 44 km^2 volcano-sedimentary aquifer in the semi-arid to arid La Aldea Valley (western Gran Canaria, Spain) has been studied, using major physical and chemical components. Current aquifer recharge is mainly the result of irrigation return flows and secondarily that of rainfall infiltration. Graphical, multivariate statistical and modeling tools have been applied in order to improve the hydrogeological conceptual model and identify the natural and anthropogenic factors controlling groundwater salinity. Groundwater ranges from Na–Cl–HCO_3 type for moderate salinity water to Na–Mg–Cl–SO_4 type for high salinity water. This is mainly the result of atmospheric airborne salt deposition; silicate weathering, and recharge incorporating irrigation return flows. High evapotranspiration produces significant evapo-concentration leading to relative high groundwater salinity in the area. Under average conditions, about 70% of the water used for intensive agricultural exploitation in the valley comes from three low salinity water runoff storage reservoirs upstream, out of the area, while the remaining 30% derives from groundwater. The main alluvial aquifer behaves as a short turnover time reservoir that adds to the surface waters to complement irrigation water supply in dry periods, when it reaches 70% of irrigation water requirements. The high seasonality and intra-annual variability of water demand for irrigation press on decision making on aquifer use by a large number of aquifer users acting on their own.

1. Introduction

Salinization is a widespread groundwater natural contamination process in arid and semiarid coastal areas, but often it is also the result of human activities, such as agricultural practices. It occurs especially where the development of irrigated crop areas has caused intensive exploitation of local groundwater resources. A number of papers dealing with groundwater salinization processes under arid and semi-arid conditions were published (Custodio, 1993; Herrera and Custodio, 2004; Jalali, 2007; Martos et al., 1999). Diverse mechanisms have been suggested to explain groundwater salinization in coastal areas: (1) seawater intrusion (Custodio and Llamas, 1976; Custodio, 2010; Cruz et al., 2011), (2) evapo-concentration (concentration by evapotranspiration) of airborne salts (Alcalá and Custodio, 2008a; Guan et al., 2010), (3) hydrogeological characteristics of the aquifer (Ben Moussa et al., 2011; Farber et al., 2007), (4) water–rock interaction, such as dissolution, leaching and hydrolysis of minerals (Abid et al., 2011; Jalali, 2007; Van der Weijden and Pacheco, 2003) and (5) human influence, such as

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return flows from irrigated agricultural activities (Almasri, 2007; García-Garizabal and Causape, 2010; Oren et al., 2004).

The La Aldea aquifer system (Gran Canaria, Canary Islands, Spain) is an example of an intensively exploited aquifer in a semi-arid to arid region where irrigated agriculture has been practiced. The environmental importance of groundwater and the economically significant agriculture in the area have fostered a series of hydrogeological and hydrogeochemical studies. The former correspond to the early 1970s, within the SPA-15 project (MOP-UNESCO, 1975) and related studies carried out by the Water Authority, the most specific ones corresponding to research projects carried out since 1992 to characterize the La Aldea aquifer system (Bejarano et al., 2003; Cabrera et al., 2006; Muñoz, 2005). A conceptual groundwater flow model was established and validated with the help of a numerical model (Cruz-Fuentes, 2008; Cruz-Fuentes et al., in press).

The study of major ions in groundwater, by means of classical methods and plots, provides relevant geochemical information on groundwater behavior and on controlling processes. The combination of these methodologies with statistical-based methods provides a consistent and objective means to study and cluster large data sets (Güler et al., 2002). Among the multivariate statistical techniques, the hierarchical clustering analysis (HCA) is a multivariate statistical technique to classify hydrochemical data and water samples into distinct groups. Scattered plots of the physical and chemical parameters were used to identify different water types, the results agree fairly well with the results of HCA to identify the main geochemical processes controlling local groundwater composition (Monjerezi et al., 2011; Morell et al., 1996; Suk and Lee, 1999), which is also the result of the present case. Moreover, complementary solute transport modeling confirms the conceptual hydrogeological and hydrogeochemical models previously established.

The main aim of this work is to address the groundwater quality problems, studying the natural phenomena and processes that govern groundwater salinization and mineralization, and the impact of agricultural activities in the sedimentary–volcanic aquifer in the western part of Gran Canaria Island. This is crucial for the sustainable management of water resources in an area of high economic value for the island, critically dependent on groundwater. Additionally it allows obtaining enough knowledge on aquifer behavior to take actions so as to address the objectives set by the European Water Framework Directive, WFD (2000/60/EC).

2. The site of study

2.1. General description

La Aldea valley, 44 km^2 in surface area, is located on the western side of Gran Canaria (Fig. 1). The valley has a flat bottom surrounded by high mountains on the north, south and east sides. In the east-west direction the valley is crossed by a main gully (La Aldea gully) and contains two secondary tributary gullies (Tocodomán and Furel), and a series of smaller tertiary gullies. The area has a dry subtropical climate characterized by alternating dry and wet periods, with important seasonal and annual rainfall variability. The average rainfall (1980–2005) is about 160 mm/year, exceeding 250 mm/year in wet years, and below 100 mm/year in dry years. Rainfall increases slightly with altitude and concentrates in October–April, with almost no precipitation in the summer.

The main use for water in the La Aldea valley is agriculture. The crop surface area reduced from 950 ha in 1992 to about 550 ha in 1996, due to the decrease of irrigation water availability, but has remained stable since then. Irrigation water is a mix of groundwater and low salinity water from upstream reservoirs. Under normal conditions reservoirs supply 70% of all irrigation needs, groundwater providing the remaining 30%. Nevertheless, during drought periods the stored surface water is not able to supply enough water and groundwater can reach up to 70% of the total supply. Reservoir water comes mainly from the Caidero de la Niña reservoir (see Fig. 1), where waters from the upstream Parralillo and Siberio reservoirs are mixed. During droughts water for population and irrigation supply is produced by means of seawater and saline groundwater desalination plants.

Tomato crops occupy more than 75% of the cultivated area, whose growth takes place mainly between September and April. They are mostly raised in greenhouses on conditioned soil, but since 1997 hydroponic cultivation is gaining popularity. Only chemical fertilizers are applied. For tomatoes, average total quantities of fertilizer applied are about 2200 to 2400 kg/ha/year approximately. The endowments are only coarsely known. Quantities and composition vary from year to year and from one farmer to another, but some common patterns exist. In the 1994–1995 hydrologic year the fertilizers applied were NPK 15-15-15 (respectively the % per weight of nitrate nitrogen, P_2O_5 (phosphorous pentoxide), and K_2O (potassium oxide), potassium nitrate and NPK 19-6-6. All these fertilizers contain up to 29% of SO_3 (sulfur trioxide).

2.2. Geological setting

A simplified geological map and a geological cross section of La Aldea gully are shown in Fig. 1. The shallow formations consist of a heterogeneous sedimentary unit composed of alluvial deposits (conglomerates, sands and subordinate silts, up to 30 m-thick in some places) and scree deposits located on the mountain flanks (trachytic–rhyolitic, phonolitic and basalts boulders, with an average thickness of 10 m). Beneath these formations there is a volcanic unit consisting of Miocene basalts with a highly weathered top. At the east side, volcanic tuffs, ignimbrites, and lava flows of trachytic–rhyolitic composition (Intra-caldera Formations) of the old volcanics filling the central caldera of the island are in tectonic contact with the Miocene basalts. Las Tabladas constitutes a residual relief located at the eastern side of the La Aldea valley, between Furel and La Aldea gullies, with a complex geology: Miocene and Pliocene detritic sediments; landslide materials that include hydrothermally altered volcanic tuffs, and Pliocene to Plio-Quaternary basalts, basanitic ignimbrites and lava flows (Cabrera et al., 2006).

Natural soils are poorly developed and contain duricrust (caliche) layers and concretions, typical of arid and semi-arid climates. Soil thickness rarely exceeds 80 cm, with large surface areas of almost bare rock. Actual agricultural soils are often built by covering natural land with soil materials transported from other parts of the island, forming terraces.

2.3. Hydrogeological setting

The La Aldea aquifer system is hydrogeologically unconfined and consists of two closely related main units: the upper sedimentary unit and the lower volcanic unit. Although the sedimentary deposits are more permeable than the basalts, both constitute a single aquifer split into two hydraulically connected sub-layers (Cruz-Fuentes et al., in press; Muñoz, 2005).

Groundwater in the different materials (basalts, scree deposits, and Las Tabladas unit) flows towards the alluvial deposits, and then westwards within the La Aldea alluvial formation (see Fig. 1). The main alluvial deposits (La Aldea deposits) and the highly altered top of basalts below behave as a water storage reservoir that is filled and emptied according to recharge and irrigation needs for agriculture, with a short turnover time of about 2 years (Cruz-Fuentes et al., in press). During drought periods, when the aquifer is intensively exploited, the water table falls below the contact of the alluvial deposits and the underlying basalts. Then groundwater in the highly altered top basalts becomes a supply complement by further depleting its storage. Scree deposits and tributary alluvial deposits behave like “wide drains” on the hillsides; they collect infiltrating surface runoff and groundwater flowing through altered basalts and recharged in the high slopes of the valley, and direct them to the alluvial formations (Cruz-Fuentes et al., in press).

The aquifer system is recharged mainly by irrigation return flows; direct infiltration of precipitation falling in the area, and water supply

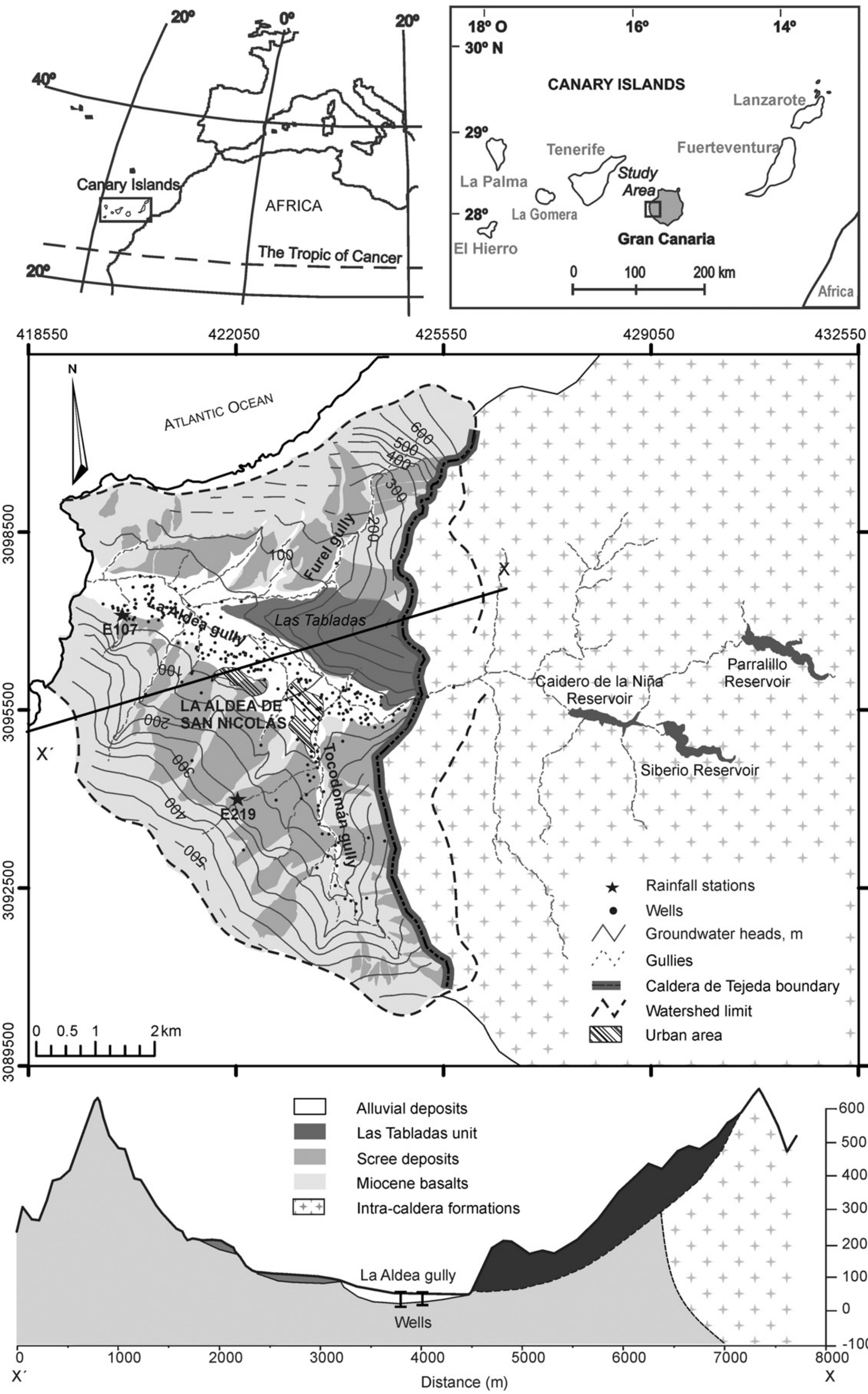

Fig. 1. Location map and spatial distribution of the main hydrogeological domains, rainfall collectors, wells and reservoirs, and groundwater head contours (m asl) map for the 1991–1992 hydrologic year as from the groundwater flow numerical model under steady conditions (Cruz-Fuentes et al., in press). Below a simplified geological cross-section is shown (modified from Cruz-Fuentes et al., in press).

networks leaks (Cruz-Fuentes et al., in press). The aquifer system also receives a small inflow from the intra-caldera area through the narrow deposits and altered basalts of La Aldea gully upstream alluvial (see Fig. 1). The aquifer natural outflow to the sea is along the short shore and from the episodic groundwater discharge into the lower part of the gully channel during the rare high recharge periods. The artificial outflow is the withdrawal from the aquifer through more than 370 large-diameter wells (2.5 to 3 m) dug in the alluvial conglomerates (see Fig. 1), albeit some of them attain and slightly penetrate the Miocene basalts below. Several permanent seepages with high salinity waters are located at the lower edge of Las Tabladas area, on top of which irrigated cropland was installed in the 1970s.

3. Materials and methods

3.1. Sampling

Groundwater samples were obtained from two field campaigns carried out in 1992 by the Island's Hydrologic Plan Office (191 samples) and in 1999 (244 samples) by the GEOVOL research team (Muñoz, 2005). Data obtained in field campaigns carried out in 1999 for non-conservative ions, such as Ca and HCO_3, may be quite altered due to difficulties in the lab and a long delay in performing the analyses. Consequently, this study is mainly based on stable dissolved ions, such as Cl, Na, NO_3, SO_4 and Mg. Analyses of local sea water; rainwater from two rainwater sampling stations in the area, at different heights operating from 2000 to 2002 (Fig. 1), and Las Tabladas seepages were added.

Electrical conductivity (EC), pH, alkalinity and water temperature were measured in the field. Na, K, Ca, Mg, Cl, SO_4, HCO_3, NO_3 and SiO_2 were determined in the laboratory using standard methods. Na and Mg excesses were calculated comparing groundwater to sea water concentrations, considering that all Cl comes from the sea. ^{18}O and ^{2}H were measured in samples of different campaigns from 1994 to 2001. The analyses were conducted in BSIA, University of Salamanca and the Autonomous University of Madrid.

The chemical composition of a theoretical irrigation water flow (without fertilizers) and an irrigation return flow (with fertilizers) has been calculated as a first approach, considering average and dry rainfall conditions, for crops on soil and under hydroponic cultivation. The approach also took into account available information on the common application of irrigation water and fertilizers and the expected evapo-concentration in the area.

3.2. Statistical analyses

Hierarchical clustering analysis (HCA) was applied to variables (physical–chemical parameters) and observations (samples), following the methods suggested by Davis (1986). The statistical computer code SPSS 19 (SPSS Inc., USA) was used by applying Ward's hierarchical method. The similarities among samples were measured by the squared Euclidean distance method. Multiple regressions were also used to establish relations of interdependence. Statistical t-tests were undertaken to check the significance of concentration differences among the clustered groups. HCA was applied to 1992 and 1999 samples with similar results. The results for the 1999 samples are only shown because they include more data.

3.3. Modeling

A three-dimensional numerical, finite-element groundwater flow model was constructed by using the MODFLOW2005 code (Harbaugh, 2005) in Visual MODFLOW graphical environment (Waterloo Hydrogeologic, 2005). It was calibrated under transient conditions, from October 1991 to September 1999. The model area was discretized by means of 50 m × 50 m cells of variable thickness, distributed in 190 rows, 201 columns and 3 layers. The surface layer corresponds to the sedimentary materials; the highly weathered top of the basalts, and several meters of the underlying altered basalts. Layers 2 and 3 (below) represent poorly altered to unaltered basalts. The model was checked with field data obtained in the 2005–2006 hydrologic year (Cruz-Fuentes et al., in press).

The chloride ion transport was modeled by using the MT3DMS code (Zheng and Wang, 1999) in Visual MODFLOW (Waterloo Hydrogeologic, 2005). The transport model was based in the three-dimensional flow model results and calibrated under steady-state for the average conditions of the 1991/1992 hydrologic year, considering an anisotropic and heterogeneous medium and assuming constant water density. The advective and dispersive/diffusive transport of chloride was modeled under conservative conditions and calibrated with 41 groundwater chloride values measured in 1992.

No-flow boundary conditions were considered at the watershed defined by the mountains and at the bottom of the model. In the alluvial deposits of the mouth of the main gully, at the littoral, the flow boundary condition was 0.45 m constant head, which is equivalent to a freshwater head of 18 m of seawater corresponding to the saturated alluvial deposits thickness (Custodio and Llamas, 1976), and the transport condition was a constant chloride concentration of 20,270 mg/L. The boundary conditions at the eastern limit of the model correspond to two recharge concentrations: one of 200 mg/L Cl, which represents the recharge produced by precipitation in the strip area between the watershed and the limit with the Intracaldera Formation, and the other one 270 mg/L Cl, which represents the small contribution from upstream through the alluvial deposits. Different recharge concentration zones were defined in the model domain according to the diverse sources of Cl: rainfall, irrigation return flows, supply and sanitation network leaks and Las Tabladas Unit seepage. A concentration factor of 3 was calculated between rainfall station E219 and a close well. This factor was applied to rainfall and irrigation water. Irrigation return flows were calibrated during the chloride transport modeling process. The water network leaks were considered negligible compared to rainfall recharge. The concentration of recharge to Las Tabladas area was 8500 mg/L Cl, and it was obtained from water samples of seepages located in this area.

4. Results

4.1. Origin of groundwater salinity

Groundwater shows highly variable salinity, reflected by the electrical conductivity (EC) ranging from 1075 to 13,330 μS/cm, after 1999 data. Water mineralization is mainly controlled by Cl and Na content. These major ionic species are positively correlated ($r = 0.87$), and their contribution to the overall chemical composition of the groundwater can be shown by the good correlation between Cl and EC ($r = 0.96$) and between Na and EC ($r = 0.92$). These results point to the dominant influence of airborne sea salts in groundwater compositional evolution. Fig. 2 shows the spatial pattern of groundwater Cl and NO_3 contents for 1992 (average year) and 1999 (dry year). Comparing the results, a significant Cl concentration increase is observed (Fig. 2a), averages increasing from 510 to 700 mg/L. In both cases the lowest Cl concentrations were found in the highest areas, which increase along groundwater flow. The highest Cl concentrations are observed at Las Tabladas foot area, reaching Cl concentrations higher than 8000 mg/L. Fig. 3 shows the logarithmic vertical column diagram (Schoeller–Berkaloff) of seepages and wells located near the Las Tabladas area. Concentrations of Las Tabladas seepages (shaded in Fig. 3) are close to that of the samples from the wells located nearest to the area (Well-8 and Well-9). The salinity of the wells located downflow from Las Tabladas progressively decreases as groundwater mixes with that contained in the alluvial materials. Wells influenced by the Las Tabladas area do not show increased SiO_2 concentration, thus discarding intense weathering of the singular volcanic materials existing there as the main source of

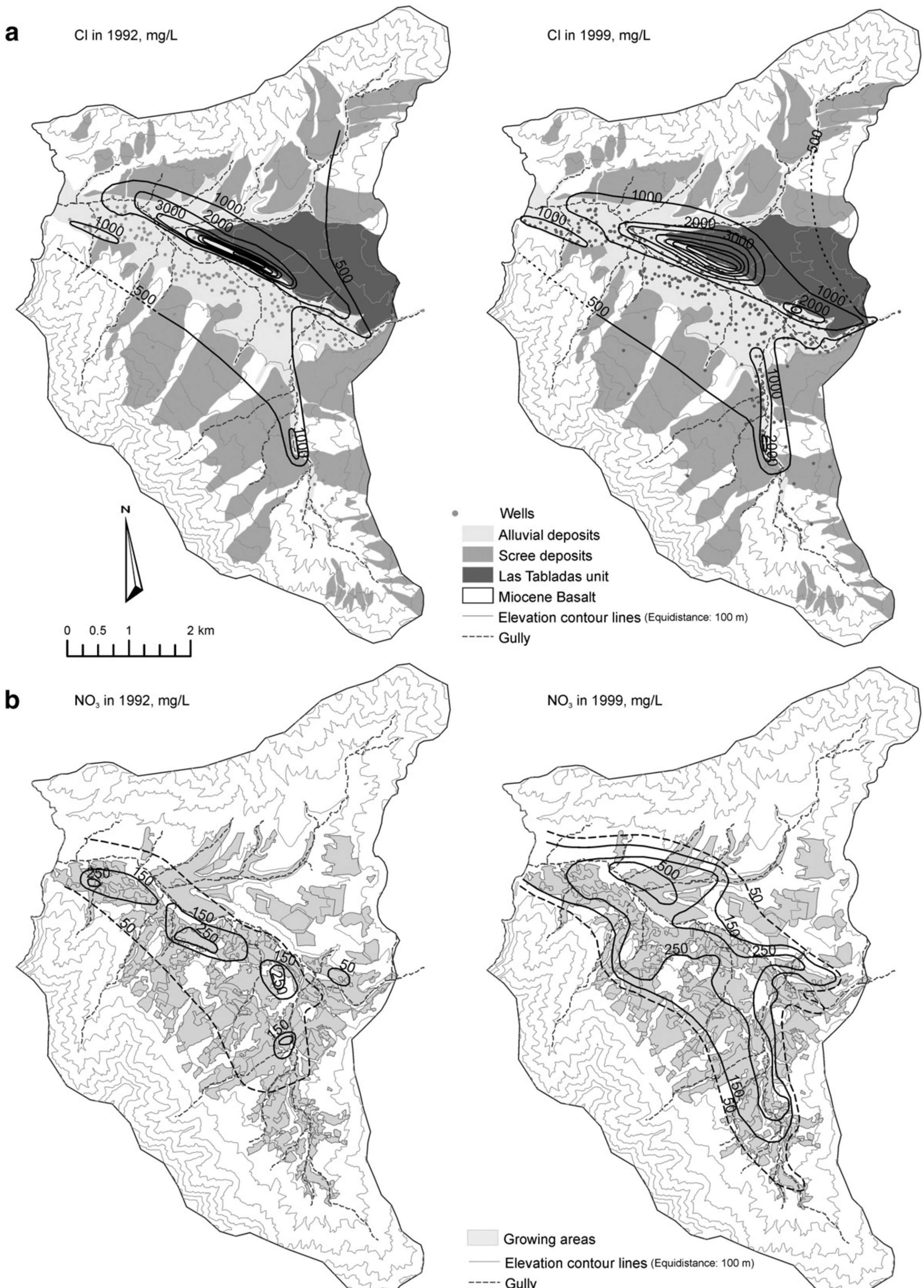

Fig. 2. Concentration isocontour lines (in mg/L) for 1992 and 1999, (a) for chloride, with geological units and sampled wells incorporated, and (b) for nitrate, with and growing areas incorporated.

solutes. rMg/rCl and rNa/rCl ratios in the seepages (r = meq/L) point to marine airborne influence in rainfall recharge, as does the rBr/rCl ratio.

The spatial distribution of modified Stiff diagrams of the 1999 groundwater samples shows the different groundwater type distribution (Fig. 4). At high altitude groundwater is of the Na–HCO_3 type, with low mineralization, which increases toward the coast. Most of the groundwater samples are of the Na–Cl type, albeit Mg–Cl, Ca–Cl and Na–SO_4 water types are also observed, pointing to some degree of water–rock interaction, especially in local low salinity groundwater. Chemical processes adding Na, Ca and Mg can result in silicate mineral

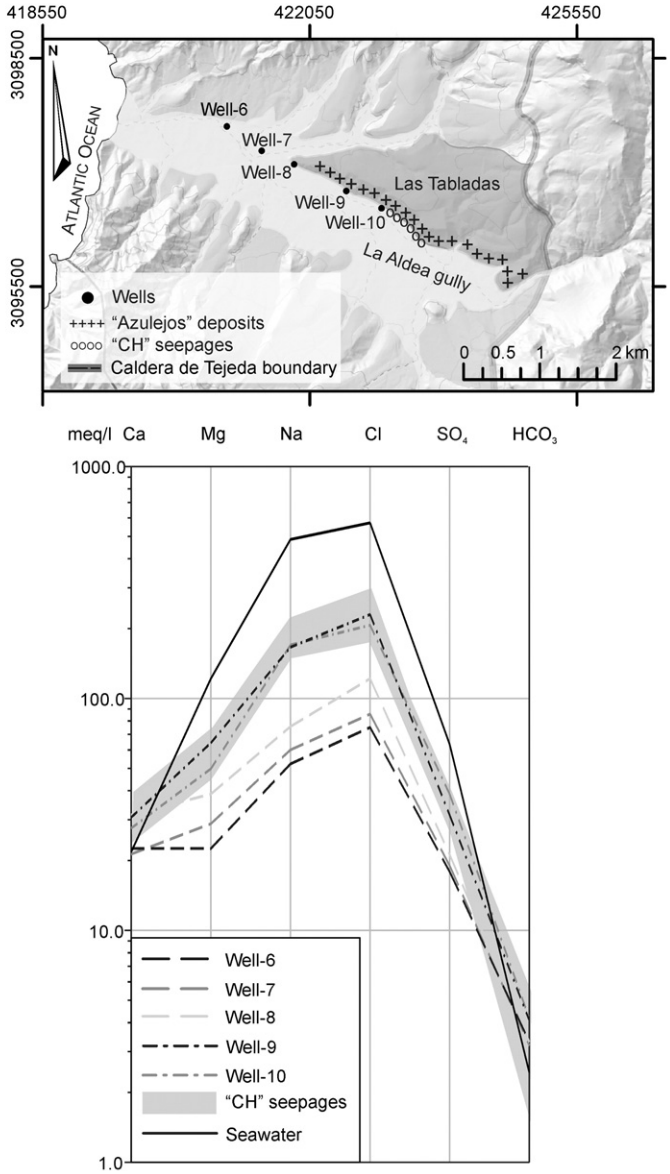

Fig. 3. Vertical logarithmic column diagram (Schoeller–Berkaloff) for water samples from the Las Tabladas seepages (designated CH) and groundwater samples affected by Las Tabladas high salinity.

weathering; Ca and Mg from basalt minerals (anorthite and forsterite) and Na from trachyrhyolitic and phonolitic rocks. High silica concentration (average value of 50 mg/L) in groundwater also shows that alkaline silicate weathering is taking place.

About 85% of the year 1999 groundwater samples show nitrate concentrations exceeding the European upper limit for drinking water of 50 mg/L (0.83 meq/L). The nitrate distribution maps for 1992 and 1999 (Fig. 2b) reveal that high nitrate concentrations appear in the lower half of the valley, where the crops are located. Values exceed 500 mg/L NO_3 where the two gullies that surround Las Tabladas merge.

The effect of agriculture on groundwater salinity was calculated by using the theoretical chemical composition of irrigation waters, adding common fertilizer endowment. Irrigation water itself contributes mainly with Cl, Na and SO_4 to groundwater salinization. Fertilizers contribute mainly with SO_4, K, PO_4 and NO_3. K and PO_4 are mostly retained by the soil and plants, as shown by the low concentrations of these ions in groundwater. For theoretical irrigation return flows, calculated SO_4 contents increase from 600 to 850 mg/L and NO_3 from 150 to 250 mg/L (from a normal to a dry year).

The theoretical irrigation return flows were compared with groundwater samples in 1999 (Fig. 5). The dashed line corresponds to theoretical irrigation return flows from crops under hydroponic cultivation in a dry year and the shadowed strip from crops on soil between the average rainfall year and a dry year. Fig. 5a is a plot of NO_3 versus Cl concentration. Many samples showing high NO_3 contents, up to 650 mg/L, correspond to wells exploiting La Aldea alluvial deposits between the central area and the coast, downstream cropland. Samples showing the highest Cl concentration (>100 meq/L), which correspond to wells in alluvium close to Las Tabladas Unit, are located between seawater dilution and rainwater evaporation lines and are not the samples with the highest NO_3 concentrations. The SO_4 versus Cl plot (Fig. 5b) shows that these two components are also related and there is an excess of SO_4 over that contributed by seawater for the corresponding Cl content due to agricultural practices. Samples were plotted below the shaded strip, but very close to it. The samples closest to the shaded strip receive water from the scree deposits, where many of the greenhouses are located.

Fig. 6a shows the $\delta^{18}O$ and δ^2H isotopic values of groundwater and also of one sample of the Caidero de la Niña reservoir water. Water lines with a slope of 8 and deuterium excess of 10‰ and 15‰ were also drawn, representing respectively the global meteoric water line (GMWL) and the local meteoric water line (LMWL) (Custodio and Naranjo, 2012). Reservoir water is affected by evaporation and becomes isotopically enriched, shifting away from the meteoric water line. Groundwater is also enriched in $\delta^{18}O$ and δ^2H, and plotted along a line with a small slope that reflects kinetic fractionation due to evaporation in the soil besides transpiration. Most of the samples tend to become isotopically heavier as Cl concentration increases (Fig. 6b).

4.2. Results of hierarchical clustering analysis (HCA)

Groundwater cluster analysis of variables was applied to EC, alkalinity, Cl, SO_4, NO_3, Na, K, Ca and Mg. The results show three main groups of variables, which have allowed the discrimination of different sources of salinization. Group A (EC–Na–K–Cl) represents the influence of airborne sea salt deposition and the weathering of trachyrhyolitic and phonolitic rocks. Group B (Ca–Mg) is attributed to weathering of basalt minerals. Group C (SO_4–NO_3) is related to agricultural influence. Alkalinity is not correlated with any of the variables.

Groundwater samples cluster into five groups, according to their chemical characteristics, when EC, alkalinity, Cl, SO_4, NO_3, Na, K, Ca and Mg are taken into account. The results of the HCA applied to groundwater samples are summarized in Table 1 and 2. Fig. 7 shows the location of the groundwater types in the area, which is similar to what is derived from the modified Stiff diagram distribution.

Group I Upper Tocodomán gully samples. Na–HCO_3–Cl type. They have the lowest ion concentration, low NO_3 (Table 1), rNa/rCl close to that of rainwater (Fig. 8c) and (rMg + rCa)/(rNa + rK) close to what is expected from phonolite and trachyrhyolite weathering (Fig. 8d).

Group II Tocodoman gully samples. Mainly of the Mg–Na–Cl–SO_4 type. rMg/rCl (Fig. 8a) higher than in seawater and in some samples higher than that of rainwater, significant Mg excess with respect to Cl, which increases with the concentration of Cl (Fig. 8b), rNa/rCl (Fig. 8c) in some samples is lower than the sea water ratio, rMg + rCa/rNa + rK closer to basalt dissolution (Fig. 8d), and high NO_3 (Table 1).

Group III Southern part of La Aldea alluvial and scree deposits. Na–Cl–SO_4 type. High SiO_2, NO_3 and SO_4 (Table 1), Na in excess with respect to Cl (Fig. 8c), and the highest rNa/rCl, which is much larger than that of sea water and rainwater.

Group IV La Aldea alluvial deposits. Two subgroups with similar hydrochemical characteristics (Na–Cl type) but independent regarding location. Group IVa, at the headwaters, have low

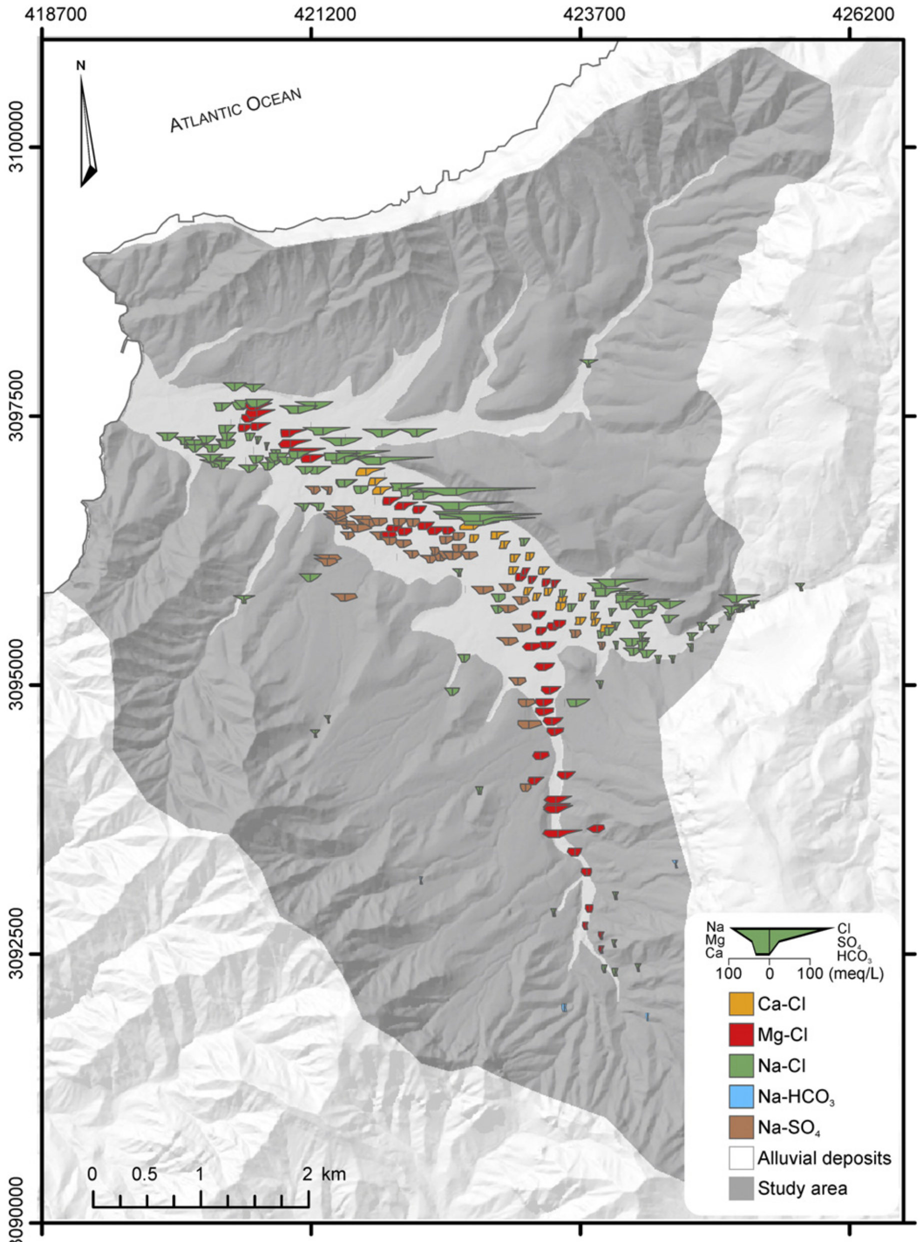

Fig. 4. Water types represented by modified Stiff diagrams for the 1999 groundwater samples.

NO_3 (Table 1) and rMg/rCl similar to seawater. Group IVb, at the valley mouth, show high SO_4 and NO_3 (Table 1). In both groups, (rMg + rCa)/(rNa + rK) is closer to that of phonolite and trachyrhyolite rock weathering (Fig. 8d).

Group V Northern part of La Aldea alluvial deposits. Influenced by Las Tabladas area. High salinity, electrical conductivity (EC) and Cl, NO_3, Na, Mg and Ca (Table 1), up to 7500 mg/L in Cl, 3700 mg/L in Na, 1800 mg/L in SO_4 and up to 500 mg/L in NO_3, a major Na default with respect to Cl (Fig. 8c), a marked Mg excess (Fig. 8b), and rMg/rCl tending to that of seawater (Fig. 8a).

4.3. Results from the steady-state chloride transport model

Transport model calibration criteria are the root mean square of concentration residuals – quadratic mean-, RMS, and the correlation coefficient between measured concentration and calculated concentration, R, where concentration residual is the difference between concentration and calculated concentration. The RMS and R of the calibration process of steady-state transport model were 73.5 mg/L Cl and 0.98, respectively. This is a good fit for the range of Cl concentrations of the study area (50–8100 mg/L).

Calibrated longitudinal, transverse and vertical dispersivities are 1 m, 0.33 m and 0.05 m, respectively. Longitudinal dispersivity is small for alluvial deposits, but it is within the values from the literature. Calibrated effective (kinetic) porosity varies between 0.08 and 0.09 for the main alluvial deposits, is about 0.08 for altered basalts, secondary alluvial deposits and scree deposits, and 0.003 for unaltered basalts, indicating mostly fissure flow with little solute exchange with the matrix.

The chloride map resulting from the transport model is shown in Fig. 9. The lowest concentrations are in the mountain highlands, where groundwater comes only from rainwater (blue colors in Fig. 9). A significant chloride contribution takes place in the central part of the study area, coinciding with irrigation returns flows from the crop

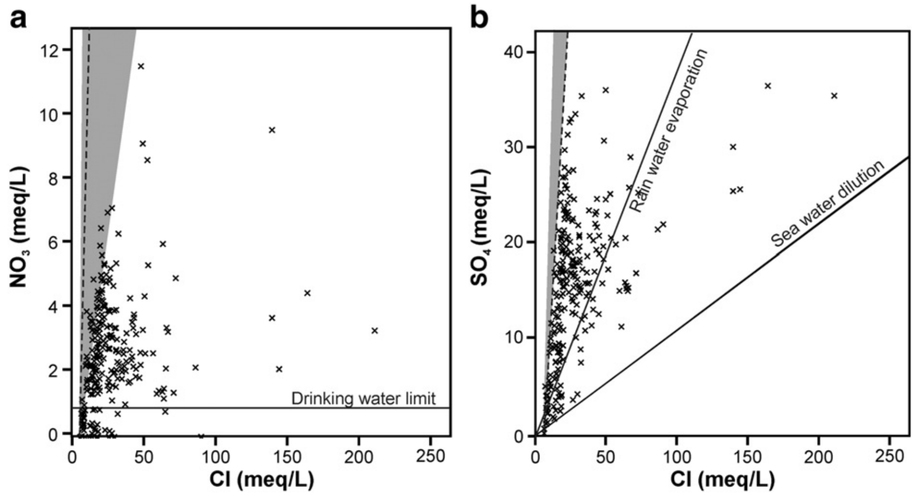

Fig. 5. Dispersion chemical plots for the 244 water samples of 1999: a) NO_3 versus Cl, b) SO_4 versus Cl. The dashed line shows the mixing of infiltrated rain water and calculated irrigation water return flows in hydroponic cultivations. The shadowed strip shows the mixing of infiltrated rain water and calculated irrigation water return flows from crops on soil for an average rainfall year (1992) and for dry year (1999). Samples with >100 meq/L Cl correspond to wells located close to Las Tabladas Unit.

area (green color area in Fig. 9). Seawater intrusion is not significant. The most relevant characteristic feature is the input of chloride-rich waters in the Las Tabladas area (red to yellow colored areas in Fig. 9), with concentrations higher than 8000 mg/L. Model calibrated Cl concentrations in irrigation return water reach 600 mg/L. This is consistent with the Cl contents calculated for irrigation return flows, which range from 500 to 700 mg/L.

5. Discussion

The assumption that groundwater salinity in La Aldea aquifer is mostly due to airborne salt deposition and evapo-concentration and related to seawater is supported by the Cl/Br ratio, which excludes evaporite salt contribution. The actual molar ratio in groundwater is somewhat greater than seawater ratio, about 655 (Alcalá and Custodio, 2008b; Custodio and Herrera, 2000). Nevertheless, this has been observed in other arid coastal areas, such as Fuerteventura Island, Canary Islands, due to a possible small chemical fractionation during airborne salt formation (Herrera and Custodio, 2004). The trend toward marine Na/Cl and Mg/Cl ratios in groundwater also points in the same direction. High evapotranspiration in the recharge process explains the conspicuous salinity increase in recharge water, both under natural conditions and as irrigation return flows. The process is accompanied by limited water–rock interaction, depending on the available soil CO_2 incorporation, which is relatively small in poorly vegetated natural soils. This explains the relatively high SiO_2 concentration and cation increase from rock weathering, dominating Na in the less basic volcanic rocks and Mg and Ca in the basalts. This increase is more visible when evapo-concentration is moderate (recharge to rainfall concentration factor of about 3 in the high and inner areas) and is masked when evapo-concentration is high, up to a factor of 20 in Las Tabladas area. Since climatic conditions are similar across the area, except in the high parts, this concentration factor depends mostly on soil water retention capacity. This is small in coarse, poor soils and half-barren rock areas, but can be large when clay is more abundant, as in alluvial areas and in Las Tabladas. This explains the high salinity of recharge water in these areas, and also the more developed duricrust (caliche) formation in the soils, currently and under past climate conditions.

The high salinity of seepages at the foot of Las Tabladas is close to somewhat diluted seawater, so early explanations pointed to relict seawater being leached by current recharge, although they are at an altitude higher than possible, relatively recent sea transgressions, being this seawater already leached by rainfall recharge considering possible old sea transgressions, or land rising. This is similar to the situation in the Amurga Massif in south-eastern Gran Canaria Island (Custodio, 1993) but different from the saline deep water in the Betancuria Massif in Fuerteventura Island (Herrera and Custodio, 2004). Another possible relict origin of salinity could be saline recharge produced under a well-developed vegetation cover, using available soil water very efficiently. This vegetation cover could have naturally disappeared due to climate modification or cut down by men since the early times of colonization after the 15th century, a common fact in many areas of the Canary

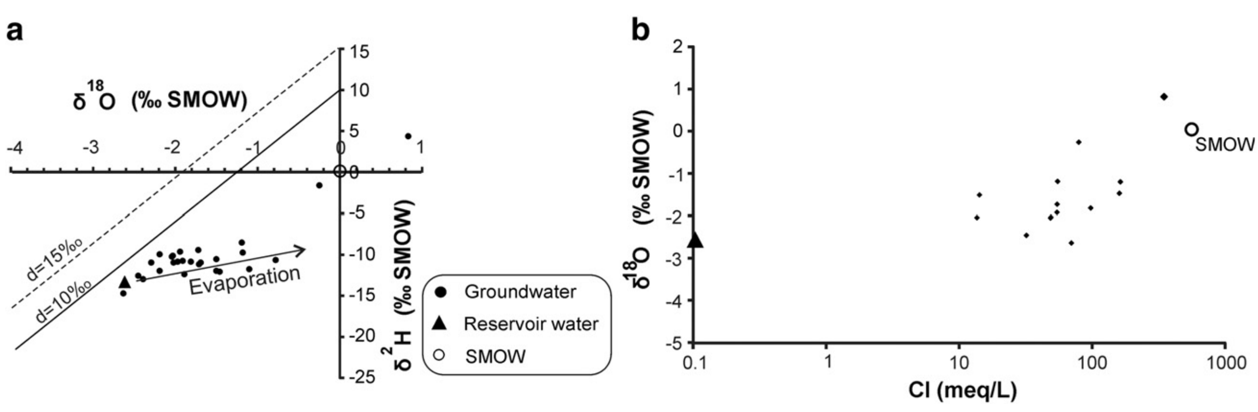

Fig. 6. Groundwater and reservoir water isotopic composition plots (modified from Muñoz, 2005): a) $\delta^{18}O$ versus $\delta^{2}H$ plot for groundwater and reservoir water, b) $\delta^{18}O$ versus Cl in groundwater.

Table 1
Chemical characteristics of groundwater of each group, for the 244 samples of the 1999 field campaign. Ion concentrations and alkalinity (as HCO_3) are in mg/L and electrical conductivity (EC) in μS/cm at 25 °C. M = mean; SD = standard deviation. pH, alkalinity and EC are those measured in the field.

Location			pH	EC	SiO_2	Ca	Mg	Na	K	Cl	SO_4	NO_3	Alkalinity
Group I (n = 16)	Upper Tocodomán gully	M	7.3	1608.9	57.7	45.9	62.8	185.2	5.5	242.2	145.3	43.5	279.9
		SD	0.3	375.6	13.1	16.9	22.8	58.5	2.0	44.6	81.6	38.8	67.1
Group II (n = 77)	Tocodoman gully and central main alluvial deposits	M	6.8	3692.9	51.2	223.8	188.3	331.4	14.9	679.4	758.1	180.6	231.7
		SD	0.3	949.1	15.0	53.4	71.6	108.4	3.9	220.1	284.9	80.1	78.3
Group III (n = 49)	South of main alluvial deposits	M	7.0	3886.7	65.3	143.5	142.5	570.0	17.1	592.6	925.5	206.2	296.4
		SD	0.3	1143.5	11.7	56.1	55.1	182.8	6.1	185.2	376.5	94.7	85.8
Group IVa (n = 18)	Headwater of main alluvial deposits	M	7.0	2921.7	40.4	108.7	92.8	395.0	15.0	683.3	324.9	44.4	233.2
		SD	0.3	1836.7	16.7	75.9	90.7	258.9	8.7	512.6	372.5	65.2	74.9
Group IVb (n = 26)	Main alluvial deposits at gully mouth	M	6.9	5006.3	49.8	177.6	181.5	713.4	25.6	1115.2	816.4	205.0	250.8
		SD	0.2	1514.7	13.0	83.7	73.7	246.4	9.8	390.0	350.8	173.6	106.6
Group V (n = 58)	North of main alluvial deposits	M	6.7	6368.1	40.6	391.6	288.1	710.8	27.4	1860.3	839.1	157.4	178.8
		SD	0.2	3519.3	11.6	178.0	140.1	614.0	14.6	1346.6	300.6	90.6	78.5

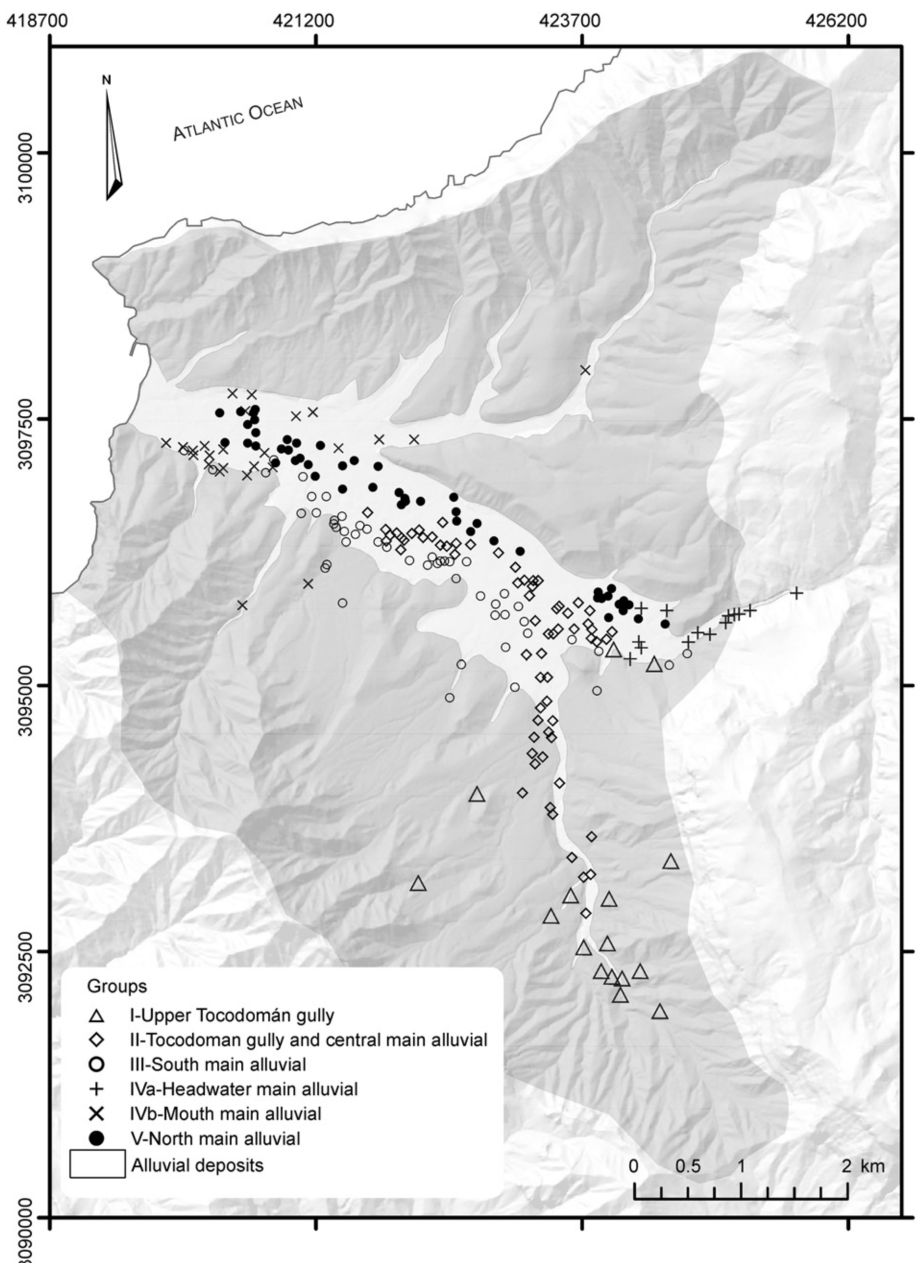

Fig. 7. Spatial pattern of the cluster groups.

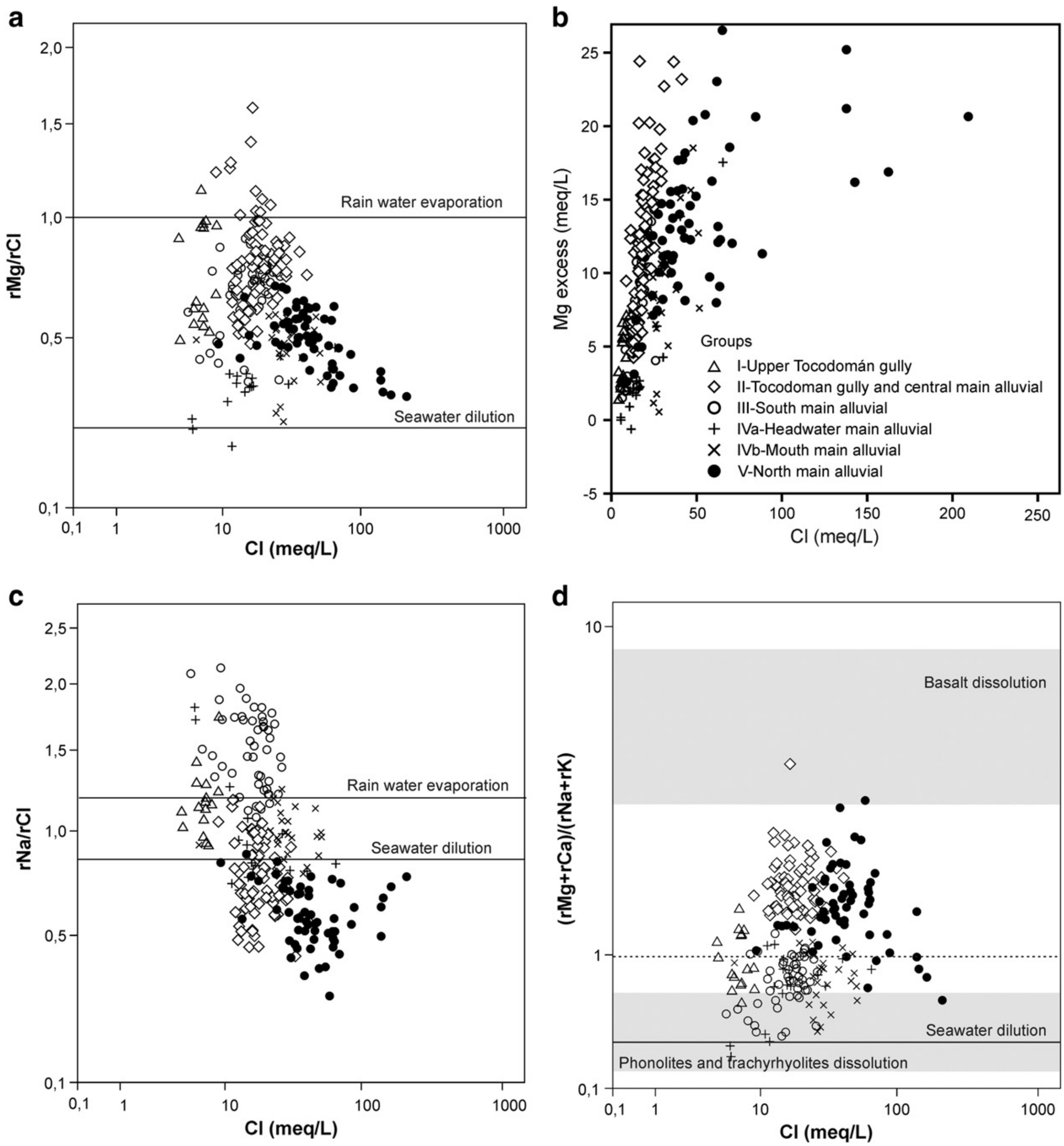

Fig. 8. Plot of ion ratios versus Cl. Chemical data of the geologic materials in the area come from rock analysis compiled from previous studies in the study area by Barrera and Gómez (1990). Rain water ratios are from the E219 station data (see Fig. 1).

Islands. Depending on porosity, thickness of the vadose (unsaturated) zone and actual recharge, the turnover time may be of less than a century to some centuries, and thus the possibility of relict existence of this saline recharge, currently pushed down by increased recharge, cannot be fully discarded. Nevertheless, this is highly improbable since recent agricultural nitrate is found in the seepages. This shows fast percolation through fissures representing a very low effective porosity. It could be possible for saline water present in the rock matrix to slowly diffuse to fissures in a continuing process. Data on seepage flow and salinity variability is not enough to discard this matrix storage although it points to recent water. A concentration factor of up to 20 could explain Cl concentration but Mg dissolution from the rock minerals is needed to achieve the concentration of Mg in the seepages. Mineral saturation indices show a possible saturation with respect to calcite (Muñoz, 2005), compatible with duricrust formation. Na default could lead to the neoformation of clays and accompanying Ca and Na exchange processes favoring calcite precipitation, although the latter cannot be confirmed due to the low reliability of Ca data. Some of the seepages have NO_3 concentrations between 50 and 100 mg/L, and up to 800 mg/L in others. In both cases, the seepages have similar concentrations of major ions, except K, NO_3 and SO_4, so some of them are affected by irrigation return flows while others are not, which points again to preferential flow paths through the 50–150 m thick vadose zone.

Recharge under the irrigated agricultural fields is dominated by return irrigation flows and their salinity depends on the proportion of reservoir and local groundwater applied, and recently on how the irrigation water salinity that is applied is modified by membrane treatment to reduce salinity. This water can be traced through its original chemical and isotopic characteristics, and the increase of SO_4 and NO_3 from mineral fertilizer application, which is also different from crops on soils and crops under hydroponic cultivation, and characterize the mixing with naturally recharged groundwater. Isotopic data on sulfate

Table 2
Synthesis of significant characteristics of HCA groundwater sample groups.

HCA groundwater sample group	Average EC (μS/cm)	Water type	Location	Observations
I	1608	Na–Mg–Cl–HCO_3 Na > Mg and Cl > HCO_3	Upper Tocodomán gully (Miocene basalts)	Rainwater recharge, no pollution affected. Na excess High Mg
II	3692	Mg–Na–Cl–SO_4 Mg > Na and Cl^- > SO_4 In 38% of samples NO_3^- > 200 mg/L	Tocodoman gully and central main alluvial deposits	High Mg High NO_3 - irrigation return flows
III	3886	Na–SO_4–Cl In 53% of samples NO_3^- > 200 mg/L	Southern part of La Aldea alluvial deposits and scree deposits	High Na. Large irrigation return flow influence. High SiO_2
IVa	2922	Na–Cl None of the samples NO_3^- > 200 mg/L	La Aldea alluvial deposits at the entrance of the gully	Infiltrated meteoric water subject to intense evapo-concentration.
IVb	5006	Na–Cl In 42% of samples NO_3^- > 200 mg/L	Furel and La Aldea alluvial deposits near the mouth of the gully	Infiltrated meteoric water subject to intense evapo-concentration. Large irrigation return flows influence.
V	6368	Na–Cl Na > Mg > Ca–Cl In 90% of samples NO_3^- > 200 mg/L	Northern part of La Aldea alluvial deposits, near Las Tabladas area	Las Tabladas influence High Na High Mg

^{34}S and ^{18}O (Muñoz, 2005) shows that the results can be explained by a mixture of marine and fertilizer sulfate, with some input of oxidized atmospheric sulfur.

All these processes produce different groundwater chemical types that can be defined and mapped by means of graphic methods and through clustering techniques, such as HCA, both yielding similar results. HCA identifies three different groups of variables allowing the identification of the four different sources of salinization presented before, although modified according to local circumstances.

The interpretation of evaporation effects with water isotopic data is complex since irrigation water is of variable salinity and isotopic composition. The positive correlation between $\delta^{18}O$ and chloride points to common processes but it is not the result of simple evaporation of a type of water, but the combination of isotopic enrichment by evaporation from a water that already may be affected by evaporative enrichment. The detailed analysis is out of the scope of this paper. Groundwater alkalinity does not correlate with salinity since different processes are involved. Alkalinity depends largely on partial CO_2 pressure in soil gas, which was not measured, but can be expected to be low in natural soils and high in intensively cultivated crop land. This explains why HCO_3 ranges from 2 to 10 meq/L, which also depends on calcite precipitation. Data on ^{13}C in dissolved inorganic carbon (Muñoz, 2005) show relatively heavy values between −9 and −14‰ $\delta^{13}C$. This can be explained considering an open system to CO_2 in the soil, under HCO_3 dominated isotopic fractionation and influence of atmospheric CO_2 on the expectable ^{13}C isotopic content. It is expected to correspond to natural C-3 plants (crassulacean plants are not the dominant ones) and crops (C-4 maize is not currently cultivated) in the area. Some data on tritium (^3H) content in groundwater (Muñoz, 2005) from 1997 and 2001 showed recent water with a decrease in content that agrees with the expectable atmospheric decay constant of about 0.13 $year^{-1}$. This means a short turnover time in agreement with the conceptual and numerical model (Cruz-Fuentes et al., in press).

Modeling has been a useful tool to check and shape the conceptual flow and solute transport models. Although the concentration of Cl in irrigation return flows obtained during the calibration process is similar to the concentration of theoretical irrigation return flows, the salinity of sampling irrigation return flow in crops on soil would reduce the uncertainty of the model, but these data are not available and are difficult to obtain. The transport model shows the relevant role of scree deposits in the hydrogeological system, as they are preferential flow pathways that favor the transfer of recharge to the alluvial deposits, but also of chloride from the irrigation return flows located thereon. Modeling shows that seawater intrusion is not significant, possibly due to the aquifer being narrow and relatively shallow at the coast, except near the coastline. In fact one well near the shore reaches 1500 mg /L Cl. The model is insensitive to molecular diffusivity since mechanical dispersivity dominates solute transport, and is only sensitive to changes in hydraulic parameters of La Aldea alluvial deposits, including kinetic porosity.

6. Conclusions

The study of major chemical solutes identifies the groundwater quality problems and establishes the natural and anthropogenic origin of salinity within an aquifer isolated from the rest of the island, in western Gran Canaria Island. The most characteristic features are that groundwater is mainly of the Na–Cl type, a large fraction of groundwater recharge derives from irrigation return flows and groundwater salinity is due to evapo-concentration of rain and irrigation water, enhanced by aridity. The combination of plots of major ions with the Hierarchical Cluster Analysis (HCA) has provided the identification of three different groups of variables which have allowed to discriminate different sources of salinization and to classify the groundwaters into five main group whose salinity is due to the combination of the various salinity sources.

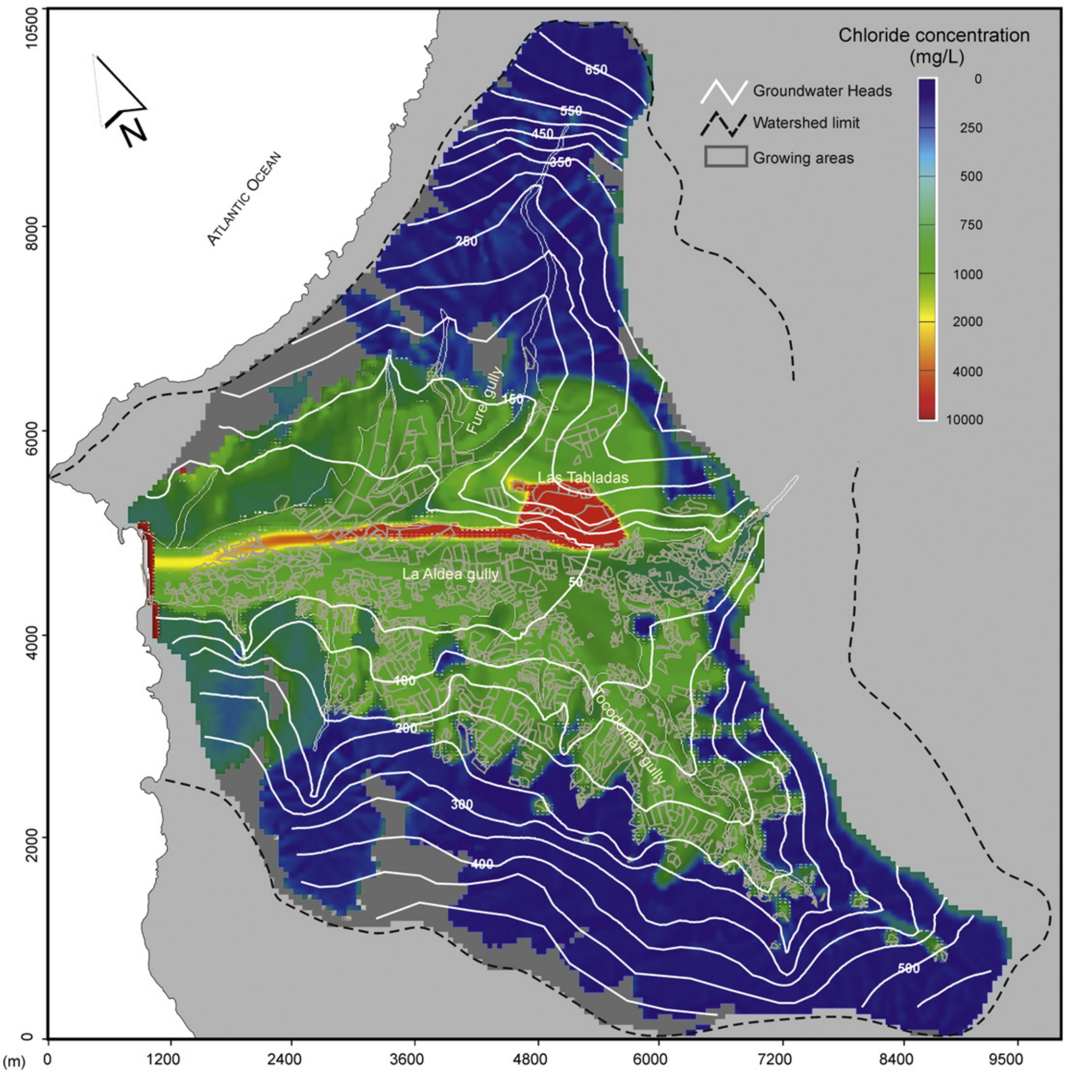

Fig. 9. Steady-state water-table map and simulated chloride concentration distribution obtained from a groundwater numerical model for 1991–1992 hydrologic year. Growing areas are inside the polygons.

Salinization is due to airborne sea salt deposition, weathering of phonolitic and basalt silicate rocks and agricultural return flows. The airborne marine influence mainly provides Cl and Na but also Mg and SO_4. Weathering is responsible for the increased concentration of Na and K (from phonolites) and Ca and Mg (from basalts). The irrigation return flows increase SO_4 and NO_3 contents. Concentrations conspicuously increase due to high evapo-concentration which is typical of semi-arid to arid conditions, and varies significantly according to soil type.

The chloride steady-state transport model has been a useful complementary tool to check and refine the hydrochemical conceptual model of the study area, to explain groundwater salinity and chemical processes, and to confirm the relevance of the scree deposits within the hydrological system as a preferential flow path facilitating the flow and the transport of chloride from irrigation return flows originated in cropland to the main alluvial deposits.

The La Aldea valley is an interesting pilot area for integrated water resources management, inside a larger area, which is the whole island. Groundwater quality considerations, as shown in this paper, must be considered for water resources management to reach an optimal use of surface and groundwater storage. Thus, it may become an example transferable to other intensively irrigated areas under arid and semiarid conditions where a similar hydrogeological and hydrochemical conceptual model applies. Similar conditions exist in other areas of the Canary Islands, such as south-eastern and southern Gran Canaria Island, western La Palma Island, southern La Gomera Island, and northern El Hierro Island, and possibly in the Cap Vert archipelago. However other non-volcanic and/or coastal areas are under similar conditions, such as those around the Mediterranean Sea, the lower and middle parts of the small river basins between the dry area of the Andes Range and the Pacific Ocean, and the arid part around the north-eastern Indic Ocean.

Current use of La Aldea aquifer may be in conflict with the good groundwater quantitative and chemical status demanded by the European WFD principles and regulations. High nitrate contents are common. Although the efficiency use of nitrate in crops could be improved and the pollution due to fertilizer application could be decreased, attaining good aquifer quantity and quality status is not compatible with local socio-economy, and implies a high cost. Should present use continue, special considerations through agreed specific legal exceptions could be needed under adequate regulations. The rationale is that this aquifer is a key part of the water resources system regulating capacity. The impact on littoral marine resources seems small to negligible. Enforcing the WFD general requirements to restore natural conditions may result in loss of water regulating infrastructure and disproportionate costs due to the special characteristics of the La Aldea aquifer system and its behavior within the local water resources system.

Conflict of interest

The authors declare that there is not any conflict of interest relating to this paper.

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