

Article

# Aquifer Recharge Estimation through Atmospheric Chloride Mass Balance at Las Cañadas Caldera, Tenerife, Canary Islands, Spain

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**Abstract:** The atmospheric chloride mass balance (CMB) method was used to estimate net aquifer recharge in Las Cañadas Caldera, an endorheic summit aquifer area about 2000 m a.s.l. with negligible surface runoff, which hosts the largest freshwater reserve in Tenerife Island, Canary Islands, Spain. The wet hydrological year 2005–2006 was selected to compare yearly atmospheric chloride bulk deposition and average chloride content in recharge water just above the water table, both deduced from periodical sampling. The potential contribution of chloride to groundwater from endogenous HCl gas may invalidate

the CMB method. The chloride-to-bromide molar ratio was an efficient tracer used to select recharge water samples having atmospheric origin of chloride. Yearly net aquifer recharge was  $631 \text{ mm year}^{-1}$ , *i.e.*, 69% of yearly precipitation. This result is in agreement with potential aquifer recharge estimated through an independent lumped-parameter rainfall-runoff model operated by the Insular Water Council of Tenerife. This paper illustrates basic procedures and routines to use the CMB method for aquifer recharge in active volcanic oceanic islands having sparse-data coverage and groundwater receiving contribution of endogenous halides.

**Keywords:** aquifer recharge; chloride mass balance; Cl/Br ratio; Las Cañadas; Tenerife

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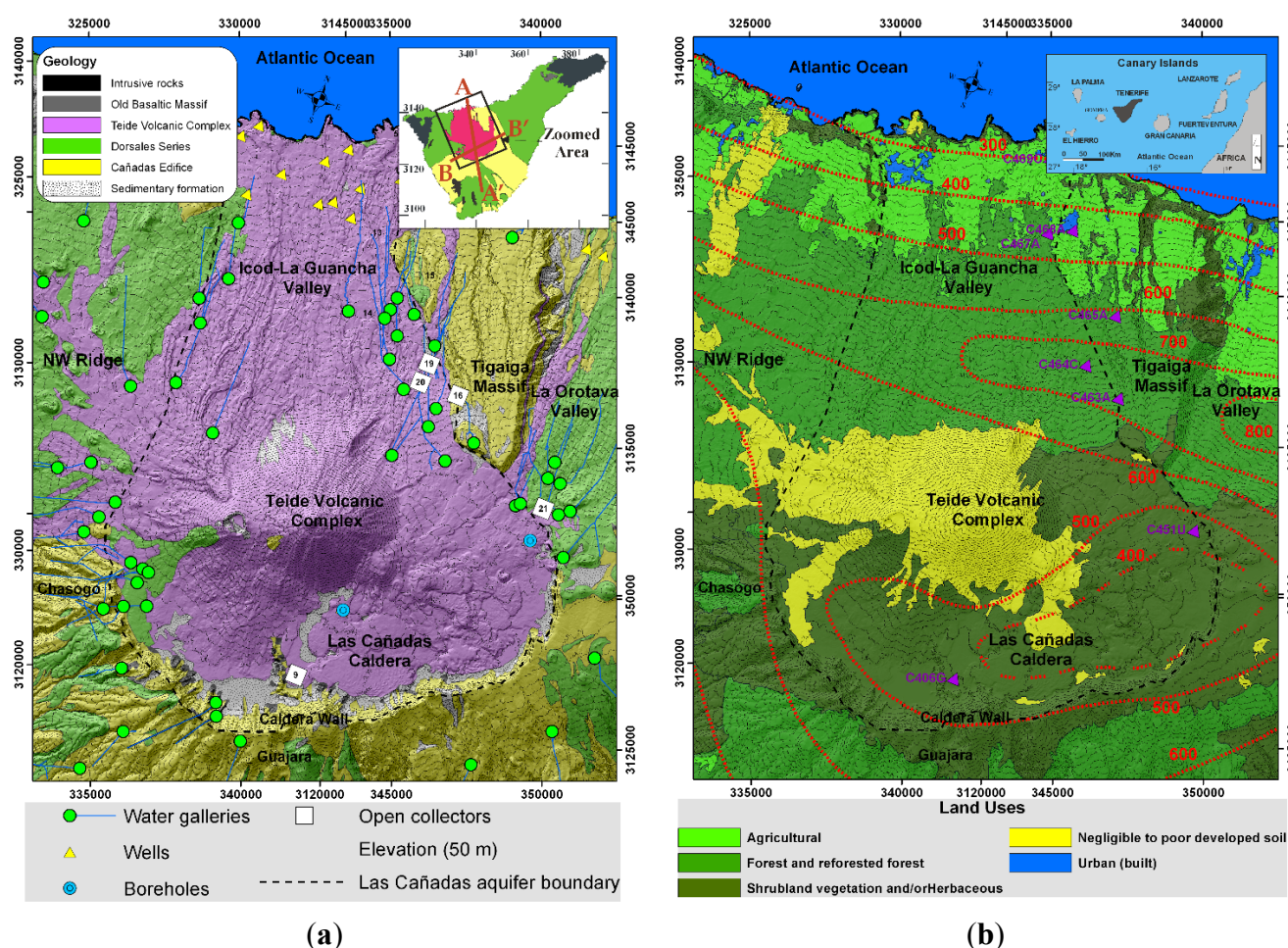
## 1. Introduction

In most oceanic volcanic islands, groundwater is the main natural freshwater resource because surface water is almost negligible due to the high permeability of the outcropping volcanic formations [1]. In Tenerife Island (Canary Islands, Spain), about 90% of total usable water resource has groundwater origin, *i.e.*, 200 Mm<sup>3</sup> of a total 226 Mm<sup>3</sup> according to 2004 official data [2]. This is a common circumstance to the other western Canary Islands [3]. The understanding of long-term balance between groundwater yield and aquifer recharge dynamics is key for the water management needed for sustainable groundwater-dependent economics in these isolated regions.

Oceanic volcanic islands are often characterized by a rugged topography that favours conditions for enhancing recharge in summit areas where precipitation and aquifer recharge rates are usually higher than in the lowlands and coastal plains [4–6]. However, the evaluation of aquifer recharge is a complex task subjected to different kinds of uncertainty [7–9] induced by the high spatial and temporal variability of precipitation [10], heterogeneities in soil and land use [11], few sampling and monitoring points [12], as well as the techniques used and the subsequent hydrological meaning and timing of estimates [13]. For instance, most aquifer recharge predictions are evaluated as difference in precipitation and actual evapotranspiration ( $E$ ) deduced from non-global models [12]. Results may be biased when compared with experimental measures [14], regional evaluations [9,10], and calibrated numerical models [11]. The combination of several techniques is a way to identify the sources of uncertainty involved [14–16].

Tracer techniques are an alternative methodology to the most widely used physical and hydrodynamic techniques for aquifer recharge evaluations ([9,13,15], and references therein). The atmospheric chloride mass balance (CMB) method is of special interest for average net aquifer recharge at different spatiotemporal scales because it does not include  $E$  in the formulae thus reducing the overall uncertainty of estimates [8,9,14,17]. For average net aquifer recharge, the CMB method is based on the steady balance of chloride mass fluxes from (1) atmospheric bulk deposition [18]; (2) surface runoff leaving the area [19]; and (3) recharge water just arriving to the water-table [15,17]. In active volcanic islands having steep topography some additional processes must be considered, such as (1) the possibility of mixing chloride flow mass rates produced by recharge rates at different elevation [20]; (2) the variable rainfall-runoff partitioning and recharge mechanisms [14]; (3) the potential contribution of non-atmospheric chloride to groundwater [21]; and (4) the potential storage of chloride in the soil and vadose zones [8,17].

This paper widens the CMB method applicability for net aquifer recharge in active volcanic islands. For this objective, atmospheric bulk deposition, groundwater, and recharge water were periodically monitored in selected points in Las Cañadas Caldera (hereafter LCC) summit area in central-northern Tenerife Island (Figure 1) during the wet hydrological year 2005–2006. Additional research was conducted to identify the potential contribution of chloride to groundwater from endogenous HCl degassing from the volcanic-hydrothermal system because this external source of chloride may invalidate the widespread use of the CMB method for aquifer recharge evaluations in Tenerife Island, as reported in other active volcanic islands [5,6,21]. The chloride-to-bromide molar (hereafter Cl/Br) ratio was an efficient tracer used to select recharge water samples having atmospheric origin of chloride [21–23].



**Figure 1.** (a) Geological map of Las Cañadas aquifer system, showing the Teide Volcanic Complex materials partially filling both the Icod-La Guancha Valley and Las Cañadas Caldera; sites cited in the text, groundwater sampling points, and open collectors are included; (b) Land-use map of Las Cañadas aquifer system and mean annual precipitation contour map; weather stations (purple triangles) operated by the Spanish Agency for Meteorology (AEMET website: <http://www.aemet.es/>) are included. Data source: Insular Water Council of Tenerife (CIATFE) [27] and Cartographic Survey of Canary Islands (GRAFCAN).

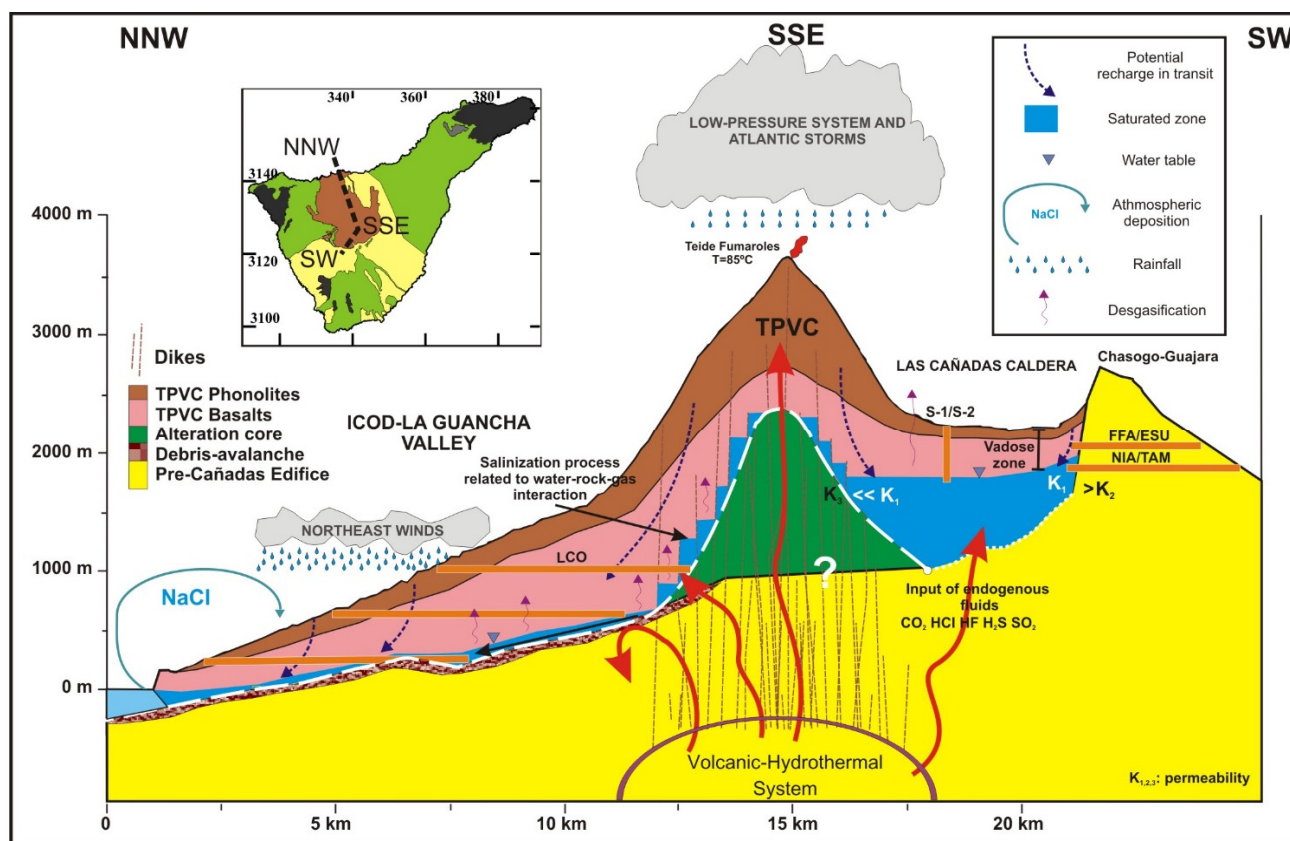
The paper is organized as follows: Section 2 describes basic characteristics of the study area, Section 3 briefly describes the CMB method and interpretative basis for its application in the study area, and Section 4 presents the main results in LCC area. Section 5 discusses the hydrological meaning of results when compared with existing independent potential recharge estimates as well as the overall CMB method applicability in volcanic areas having contribution of endogenous halides to groundwater. Section 6 concludes with practical remarks for groundwater resources planning in Tenerife Island.

## 2. Study Area

Las Cañadas aquifer system is a 216-km<sup>2</sup> steep area on the northern side of Tenerife Island that ranges from the sea to the summit of the Teide Volcano. Las Cañadas aquifer is contained within the collapse-forming LCC, the Teide-Pico Viejo Volcanic Quaternary Complex (hereafter TPVC), and the landslide-formed Icod-La Guancha Valley (hereafter IGV) ([24], and references herein) (Figure 1a). The huge elevation from the coast to the Teide Volcano (peak elevation, 3718 m a.s.l.) induces remarkable climatic differences at the Las Cañadas aquifer. In spite of the geographical proximity to the Sahara Desert, air temperature in the coast and mid-slope of windward Tenerife is relatively mild during the whole year. The climate is dominated by humid trade winds from the northeast, which blow more than 90% in time in summer and less frequently in winter. In winter, low-pressure and oceanic storms also affect Tenerife Island weather ([25], and references therein). At the IGV, mean annual temperature varies in the 15–20 °C range while precipitation increases upslope from 300 mm·year<sup>-1</sup> near the coast to 700 mm·year<sup>-1</sup> on the mid-slope (Figure 1b) due to the intersection of the north-easterly trade winds. Above 1000–1500 m a.s.l., thermal inversion occurs and weather conditions becomes drier most of the year; precipitation occurs 43 days a year in average, 12 of them as snow [26]. Average annual precipitation in LCC ranges from 500 mm in windward areas to less of 300 mm in the center (Figure 1b), mainly from October to April; yearly precipitation may reach 1000 mm in wetter periods.

LCC is a 128-km<sup>2</sup> semi-elliptical, sparsely vegetated (Figure 1b) endorheic basin opened to the sea by the north side at the summit of the Las Cañadas aquifer system. LCC is considered the largest groundwater reserve in the island [27]. The TPVC Quaternary volcanic deposits lining LCC induces high fissuring and poorly developed soils of 0.2–0.3 m in thickness [28,29]. These conditions favour fast infiltration of rainfall and snow melt, null temporal storage of chloride in the soil and vadose zones, and negligible runoff [27,30].

The hydrogeological behaviour of the high-permeability TPVC deposits contrasts with the low-permeability Las Cañadas Edifice bedrock, the hydrothermal alteration core below TPVC, and the dyke-intrusion network across them [31,32] (Figure 2). Low-permeability materials act as barriers to the groundwater flow, thus allowing the groundwater storage in the high-permeability summit caldera above 1800 m a.s.l. [30,32,33] (Figure 2). The existence of a low-permeability clay-rich debris-avalanche deposit at the IGV bottom related to the landslide origin of this valley [24,31,34,35] enhances the relatively fast groundwater flow along this valley from TPVC and LCC to the northern coast (Figure 2). This conceptual hydrogeological functioning of Las Cañadas aquifer [33] is in accordance with the conceptual hydrogeological functioning proposed by [3,36] for this type of volcanic islands [5,6,37,38].



**Figure 2.** Conceptual hydrogeological model of Las Cañadas aquifer system, including Las Cañadas Caldera, Teide-Pico Viejo Volcanic Complex (TPVC), and Icod-La Guancha Valley areas, after [33]. Main hydrogeological processes affecting groundwater dynamics and hydrochemistry are shown.

The physical-chemical characteristics of groundwater discharged from galleries suggest that most of groundwater flowing from TPVC and LCC to surrounding areas occurs through the IGV [33]. Galleries or water mines are around 2 m × 2 m man-made sub-horizontal drains, usually with two or more branches and some-kilometers long (up to 6 km), depending on the distance needed to reach the aquifer saturated zone [1,2,33]. Groundwater hydrochemistry in LCC is sodium bicarbonate-rich with electrical conductivity above 1000  $\mu\text{S cm}^{-1}$  [33]. Hydrochemical processes are related to the emission of reactive deep-seated volcanic gases such as  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{SO}_2$ , and  $\text{HCl}$  from the volcanic-hydrothermal TPVC system [33,39–41]. Diffusion of these gases induce rock weathering, and enrichment in total dissolved inorganic carbon (TDIC) and in some chemical species such as  $\text{Cl}^-$ ,  $\text{HCO}_3^-$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{SiO}_2$  [42–44].

Water table depth varies in the 300–400-m range below the LCC surface (Figure 2), thus discarding direct evaporation from the saturated zone, as corroborated through similar signatures of  $^{18}\text{O}$  and D stable isotopes in precipitation and recharge water [33]. The water-table geometry was inferred from self-potential and audiomagnetotelluric data [32]. Data showed two main eastern and central-western groundwater systems divided by the collapse caldera limit with different water-table trends, as recorded by CIATFE in scientific boreholes S-1 and S-2, respectively [30,45]. As plotted in Section 4.3, since 1994, the borehole S-1 records a drawdown oscillating trend of a few meters while the borehole S-2 records a drawdown linear trend around 0.12 m per month in average. These divergences are induced

by a different basement geometry and testable influence of galleries draining groundwater nearby the borehole S-2 in the eastern system (Figure 1a) [30]. Tens of galleries drain the LCC aquifer at different depths and elevations (Figure 1a); no pumping wells yield the LCC aquifer.

Average transit time of infiltrated rainfall through the vadose zone is about 2 months, as deduced by [30] through water-table fluctuation techniques [46]. A good correlation between input precipitation events recorded at LCC and subsequent two-month delayed water-table rises in borehole S-1 was clearly observed in late autumn and winter rainy periods [30,45]. Groundwater response is a function of the saturation degree of the vadose zone as well as the rainfall distribution and intensity [30].

### 3. Methods and Interpretative Basis

#### 3.1. Atmospheric Chloride Mass Balance (CMB) Method

The atmospheric chloride mass balance (CMB) is an appropriate, widely used method for net aquifer recharge in volcanic island environments [5,6,20,47,48]. Net aquifer recharge means the groundwater fraction that remains in the aquifer after discounting groundwater up-take by direct evaporation and deep-rooted vegetation from direct rainfall and runoff infiltration through the vadose zone after some delay, smoothing out the variability inherent to rainfall events [17,49,50]. In what follows, net aquifer recharge is expressed simply as recharge.

Chloride ion (hereafter  $\text{Cl}^-$  is expressed as Cl) is a conservative ideal tracer to perform mass balances because it does not undergo significant exchange with the environment, is chemically stable and highly soluble, has a known origin in most cases, and can be accurately measured by using common analytical methods [17,21]. The main atmospheric chloride sources are the marine aerosol dissolved in precipitation, salts contained in terrestrial dust, and natural and artificial volatile chloride compounds [51,52].

For a long enough period (e.g., one hydrological year) under steady-state conditions, in which the temporal storage of chloride in the soil and vadose zones can be assumed negligible, the CMB method is based on the steady balance of chloride mass fluxes from (1) atmospheric bulk deposition, which includes both chloride dissolved in precipitation and from atmospheric dust and marine aerosols [18]; (2) surface runoff leaving the area [19]; and (3) recharge water just arriving to the water-table [15,17]. The CMB method can be expressed as:

$$\sum (P_i \cdot C_{P_i}) = \sum (R_i \cdot C_{R_i}) + \sum (S_i \cdot C_{S_i}) \pm \sum F_i \quad (1)$$

where  $P$ ,  $R$ , and  $S$  are precipitation, recharge, and surface runoff for the successive  $i$  events sampled, respectively;  $C_P$ ,  $C_R$ , and  $C_S$  are the average Cl concentration in the corresponding  $P$ ,  $R$ , and  $S$   $i$  water samples, respectively; and  $F$  is other non-atmospheric chloride mass fluxes adding to the groundwater such as endogenous halides in volcanic areas receiving deep warm gases. For a yearly balance  $P$ ,  $R$ , and  $S$  are expressed in consistent units as  $\text{m} \cdot \text{year}^{-1}$ ;  $C_P$ ,  $C_R$ , and  $C_S$  as  $\text{g} \cdot \text{m}^{-3} \equiv \text{mg} \cdot \text{L}^{-1}$ ; and the Cl mass fluxes  $A$  ( $=P \cdot C_P$ ),  $R \cdot C_R$ ,  $S \cdot C_S$ , and  $F$  as  $\text{g} \cdot \text{m}^{-2} \cdot \text{year}^{-1}$ . Actual evapotranspiration ( $E$ ) is not involved into CMB equations because it is chloride-free water vapour [8].

### 3.2. The Chloride Mass Balance (CMB) Method Application in the Study Area

Because the CMB method may present limitations in some disadvantageous hydrogeological contexts [53,54], some additional processes must be considered for recharge evaluations in Las Cañadas aquifer system, such as (1) the possibility of mixing chloride flow mass rates produced by recharge infiltrated at different elevations [20]; (2) the variable rainfall-runoff partitioning and recharge mechanisms, land use, and soil-vegetation conditions with elevation [14]; (3) the potential contribution of non-atmospheric chloride to groundwater from endogenous halides and human activities [21]; and (4) the potential storage of chloride in the soil and vadose zones [8,17].

In low and mid-slope areas, along the IGV, most of the groundwater sampled in deep penetrating galleries integrates the variable chloride mass flux produced by recharge infiltrated at different elevations (Figure 2). Groundwater is highly mineralized as result of a significant rock-water interaction enhanced by long residence times and subsequent input of warm and reactive volcanic gases contributing chloride to groundwater; intensive agriculture may be an additional source of chloride to groundwater. Tritium and radiocarbon data suggest long residence time in the order of hundreds to thousands years for some of that water [55,56]. The limited number of sampling points having a traceable atmospheric origin of chloride prevents the usage of this water for recharge evaluations.

In summit areas, LCC nevertheless meets conditions to use the CMB method for recharge evaluations. Groundwater from recharge infiltrated in that site has a traceable atmospheric origin of chloride, as corroborated by similar signatures of  $^{18}\text{O}$  and D stable isotopes in recharge water and precipitation [33]. Recharge in transit through the vadose zone just above the water-table can be sampled in some galleries draining the vadose zone to avoid the diffusion of endogenous halides to groundwater that occurs in the saturated continuous media. For practical purposes, this recharge in transit can be assumed a reliable proxy of net aquifer recharge having a less smoothed and delayed signal of atmospheric chloride [14,17], and negligible contribution of endogenous halides [33]. Diffuse and variable combinations of diffuse and preferential recharge mechanisms are intersected and drained by galleries, thus being these water points reliable to collect bulk chloride mass flow of different recharge mechanisms before arriving to the saturated zone.

In LCC, some specific hydrological boundary conditions described above were of assistance in evaluating recharge, such as (1) direct evaporation from the saturated zone is null; (2) surface runoff leaving the area is null, thus  $S \cdot C_S = 0$ ; (3) fast infiltration induces negligible temporal storage of chloride in the soil and vadose zones; and (4) long-term  $F$  due to direct diffusion of halides to groundwater can be assumed negligible. So, Equation (1) can be expressed as:

$$\sum(P_i \cdot C_{Pi}) = \sum(R_i \cdot C_{Ri}) \quad (2)$$

For the preparation of yearly  $A$ , successive monthly  $A_i = P_i \cdot C_{Pi}$  values were added. Sampling frequency was programmed to cover the average percolation time of about two months reported by [30], as in [14,16]. Some gaps in data sets were filled by proportional correction [18]; for a full  $n$ -day period having an analysed  $P'$  fraction of total  $P$  it was assumed that  $A^C = (365P/nP)A^M$  where superscripts M and C denote measured  $A$  in the  $n$ -day period and calculated yearly  $A$ , respectively. This correction is easy but if gaps tend to correspond to a given period of the year or omit exceptional events, yearly results may be biased [9,50]. The  $C_R$  data from successive monthly and bimonthly  $i$

samples in galleries were averaged by the corresponding discharge flow to deduce average-weighted yearly values [14].

The CMB method application in the study area was based on (1) short percolation time through the vadose zone [30]; (2) steady conditions in sampling points with no-forced trends induced by pumping and climate in flow and  $C_R$  [33]; and (3) traceable similar atmospheric origin of the average-weighted  $C_P$  and  $C_R$  through the use of the Cl/Br ratio [21–23].

The  $C_P$  and  $C_R$  concentrations in filtered unacidified rainwater and groundwater samples were analysed by the Environmental Research Division Laboratory (ITER) with a DIONEX DX-500<sup>®</sup> high-performance liquid (anionic) chromatograph. Regarding to the precision of the analyses, relative standard deviations for the peak areas were below 2%. Analytical detection limit was 0.01 mg L<sup>-1</sup> for Cl and Br.

## 4. Results

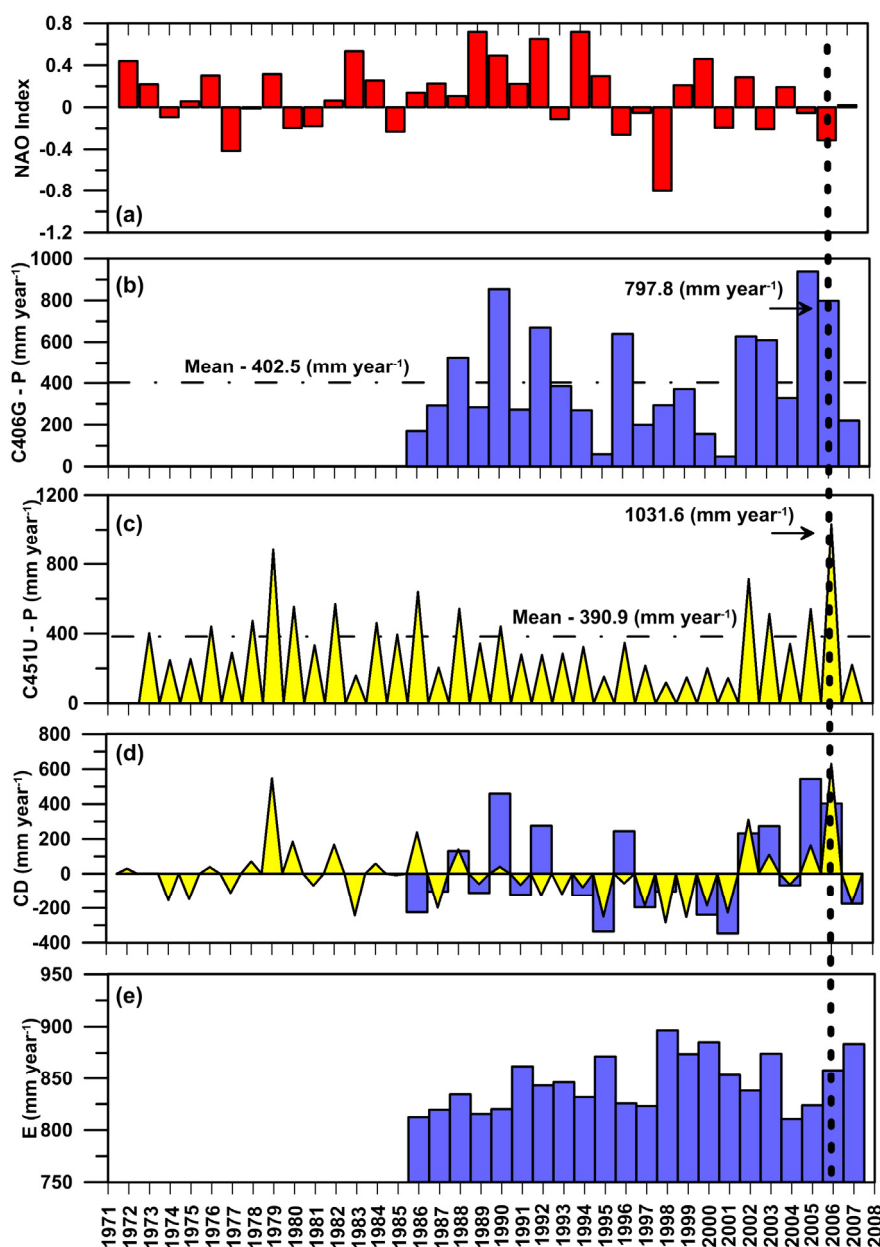
### 4.1. Hydrological Regime of the Study Area

The hydrological regime in the LCC area was deduced from the 23-year C406G and 35-year C451U AEMET weather stations time series (Figure 1b). Average yearly precipitation ( $P$ ) was 402.5 mm and 390.9 mm in C406G and C451U stations, respectively (Figure 3b,c). Cumulative deviation from average yearly  $P$  (Figure 3d) showed five-year long positive and negative phases which coarsely follow the decadal North Atlantic Oscillation cycles (Figure 3a). Because only daily records of  $P$  and temperature were available from 1986 onward, the non-global Hargreaves model was used for  $E$ , as proposed by FAO [57]; average yearly evapotranspiration ( $E$ ) was 845.6 mm in C406G station (Figure 3e). Samplings and field surveys programmed to evaluate recharge were carried out in the wet hydrological year 2005–2006 (Figure 3). In this year, yearly  $P$  recorded in C406G and C451U stations was 797.8 mm and 1031.6 mm, respectively. In the year 2005–2006, an arithmetic mean of 914.7 mm year<sup>-1</sup> was the yearly  $P$  established in the LCC recharge area with a yearly  $E$ -to- $P$  (hereafter  $E/P$ ) ratio around 1.08.

### 4.2. Atmospheric Chloride Bulk Deposition

Yearly atmospheric chloride bulk deposition in the LCC area was estimated by adding successive monthly precipitation records and the corresponding average chloride concentration measured in five non-permanent open collectors installed from 1316 m a.s.l. to 2159 m a.s.l. in the LCC recharge area (Figure 1a, Table 1). A full description of monthly values, sampling procedures, and statistical treatment of data is included in [33].

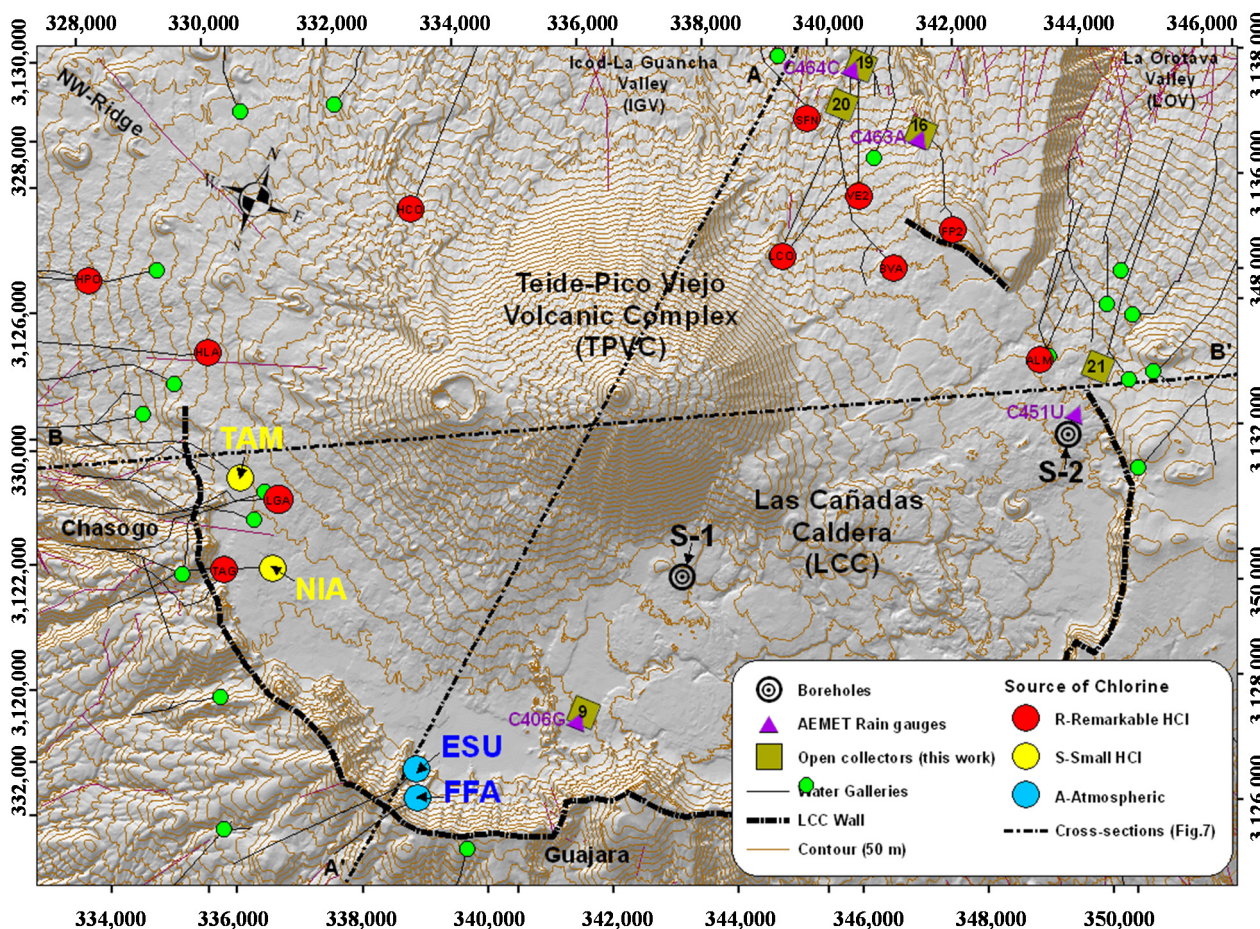
Precipitation measured in open collectors 9 and 21 was 729.2 and 680.7 mm·year<sup>-1</sup>, respectively. These figures are slightly lower than precipitation recorded in nearby C406G and C451U weather stations (Figure 3). The difference is attributable to failures in collecting rainwater samples in the open collectors. So arithmetic mean  $P$  = 914.7 mm·year<sup>-1</sup> from C406G and C451U weather stations and average-weighted  $C_P$  = 5.37 mg·L<sup>-1</sup> from collectors 9 and 21 (Table 1) were used as input data to calculate recharge in the year 2005–2006. Average-weighted Cl/Br = 255 is probably a biased value because Br was only measured in three rainwater samples in collectors 9 and 21.



**Figure 3.** Hydrological regime in the LCC area from hydrological years 1971–1972 to 2007–2008. (a) Normalized North Atlantic Oscillation (NAO) index (NAO website: <http://www.ncdc.noaa.gov/teleconnections/nao/>); (b) yearly precipitation ( $P$ ,  $\text{mm}\cdot\text{year}^{-1}$ ) in C406G weather station at 2160 m a.s.l.; (c) yearly precipitation ( $P$ ,  $\text{mm}\cdot\text{year}^{-1}$ ) in C451U weather station at 2118 m a.s.l.; (d) cumulative deviation from average yearly precipitation ( $CD$ ,  $\text{mm}\cdot\text{year}^{-1}$ ) in C406G and C451U stations; and (e) yearly evapotranspiration ( $E$ ,  $\text{mm}\cdot\text{year}^{-1}$ ) in C406G station. Horizontal dashed lines correspond to average yearly precipitation in C406G and C451U stations. Vertical dashed line corresponds to yearly precipitation recorded in the year 2005–2006.

#### 4.3. Average Chloride Concentration in Recharge Water

Selective sampling were programmed in the year 2005–2006 to deduce average-weighted yearly  $C_R$  in recharge water and groundwater having different residence times, water-rock interactions, and contribution of endogenous chloride. Data from the literature were also used to enlarge data sets, in particular from the CIATFE hydrochemical database [33]. A total of 16 sampling points were selected in the LCC area (Figure 4) attending to the groundwater flow type and the origin of chloride deduced in previous research [21,22,33] by means of  $C_R$  and Cl/Br values, as defined in Section 3.2 (Table 2).



**Figure 4.** Selected groundwater sampling points in the Las Cañadas Caldera area, clustered by groundwater flow type and origin of chloride by means of  $C_R$  and Cl/Br values as in Table 2. Open collectors for atmospheric bulk deposition and AEMET weather stations are showed.

The galleries ESU and FFA are located just above the water table. They drain potential recharge in transit bypassing a 150-m thick vadose zone [30,33] as combination of diffuse infiltration in porous media and preferential percolation through fissures [33,58], giving average-weighted yearly  $C_R = 7.73 \text{ mg} \cdot \text{L}^{-1}$  and Cl/Br = 144 (Table 2). Tritium contents in ESU ( $0.4 \pm 1.1$  Tritium Units) and FFA ( $3.0 \pm 1.1$  Tritium Units) determined by [55] in the year 1984 corroborates a predominant contribution of modern recharge.

**Table 1.** Yearly atmospheric chloride bulk deposition data from 5 non-permanent open collectors in the Las Cañadas Caldera area.

Station	Coordinates		Elevation m a.s.l.	Sampling Period		<i>n</i> days	<i>P</i> mm	<i>P'</i> mm	Cl mg L <sup>-1</sup>	Br mg·L <sup>-1</sup>	Cl/Br	<i>A</i> <sup>M</sup> g·m <sup>-2</sup>	<i>A</i> <sup>C</sup> g m <sup>-2</sup> ·year <sup>-1</sup>
				From	To								
9	−16.3735	28.1328	2149	28 September 2005	17 October 2006	384	729.2	653.3	5.62	0.16	145	3.67	3.90
16	−16.3640	28.1940	1711	28 September 2005	04 October 2006	369	636.0	590.0	5.50	0.02	890	3.25	3.46
19	−16.3731	28.2010	1316	22 September 2005	04 October 2006	377	552.9	552.6	5.91	0.04	300	3.28	3.19
20	−16.3632	28.1937	1475	22 September 2005	04 October 2006	377	676.9	673.9	3.50	0.03	726	2.34	2.28
21	−16.3359	28.1817	2059	28 September 2005	17 October 2006	383	680.9	636.7	5.18	0.01	368	3.30	3.36

Notes: *P*—Total precipitation recorded in the study period; *P'*—Fraction of analysed *P*; *A*<sup>M</sup>—Measured atmospheric chloride bulk deposition in the *n*-period monitoring; *A*<sup>C</sup>—Calculated yearly atmospheric chloride bulk deposition as  $A^C = (365P/nP)A^M$ .

**Table 2.** Chloride and bromide content, and Cl/Br ratio in groundwater in the Las Cañadas Caldera area. Sampling points were clustered into 3 groups attending to groundwater flow type and the origin of chloride.

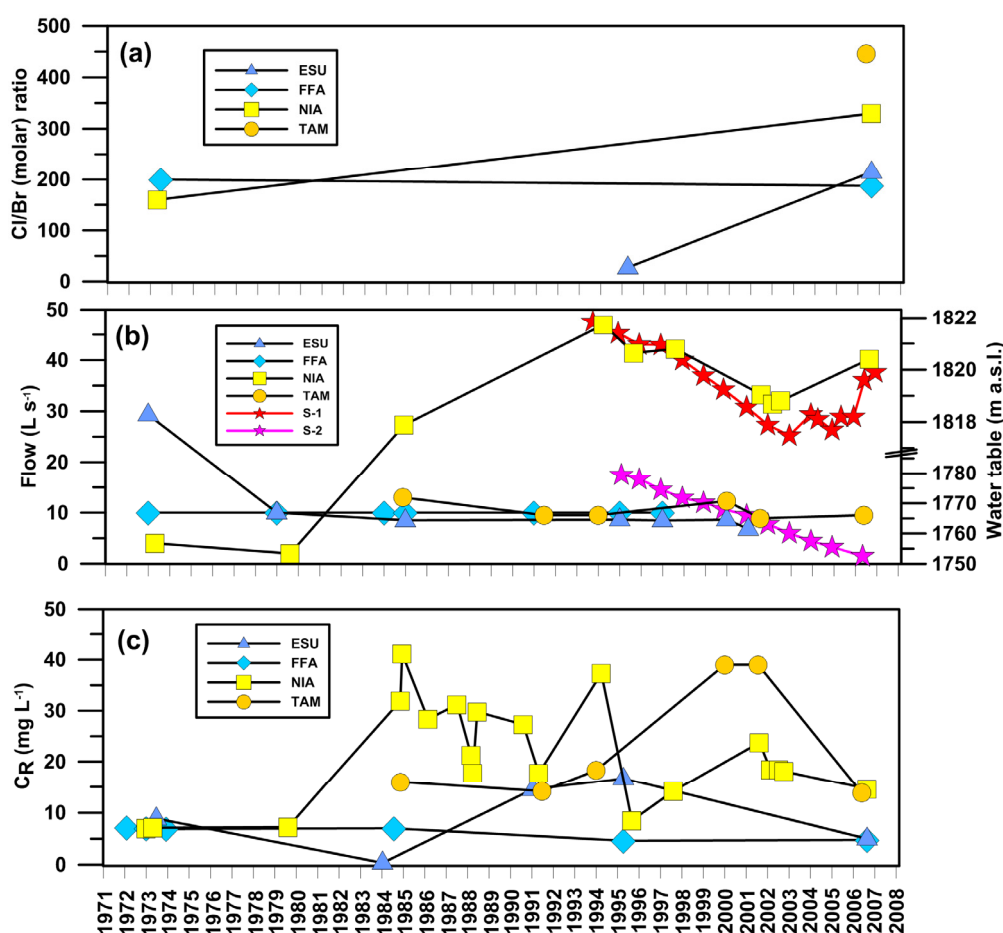
Groups	<i>n</i>	Flow (L·s <sup>-1</sup> )	Cl			Cl/Br			Br			Recharge Area Elevation (m a.s.l.)	Outlet Discharge Elevation (m a.s.l.)	Source of Data	Source of Chloride
			M	±1σ	CV	M	±1σ	CV	M	±1σ	CV				
1-Recharge	9	0.1–29.3	7.73	4.58	0.59	144	87	0.61	0.04	0.16	0.25	2074–2184	1895–2040	[1,2]	A
2-Shallow	16	2.0–47.0	20.95	11.20	0.53	338	144	0.43	0.09	0.01	0.11	2077–2133	1525–1779	[1,2]	S
3-Deep	11	4.0–237.2	25.55	11.20	0.44	740	207	0.28	0.08	0.03	0.38	1533–2115	790–1780	[1]	R

Notes: Recharge water (Group 1) includes ESU and FFA galleries; Shallow groundwater (Group 2) includes NIA and TAM galleries; and Deep groundwater (Group 3) includes ALM, BVA, FP2, HLA, HCO, HPO, LCO, LGA, TAG, SFN, and VE2 galleries, after [33]. See location of sampling points in Figure 4. M—Average-weighted yearly value; ±1σ—Standard deviation of M; CV—Coefficient of variation of M. For Cl, M and ±1σ in mg·L<sup>-1</sup>; for the rest, dimensionless. Source of data: 1—[33]; 2 the CIATFE hydrochemical database, in [33]. Source of chloride: A—Atmospheric only; S—Small contribution of volcanogenic halides; R—Remarkable contribution of volcanogenic halides.

The NIA and TAM galleries drain the shallow water-table [33], giving average-weighted yearly  $C_R = 14.96 \text{ mg}\cdot\text{L}^{-1}$  and  $\text{Cl}/\text{Br} = 413$ . These figures are induced by a mixture of recharge in transit in low-water-table periods and short-turnover-time groundwater receiving contribution of endogenous chloride in high-water-table periods (Table 2).

Peripheral galleries penetrating from outside to the saturated zone at different elevation and depth provided average-weighted yearly  $C_R = 25.55 \text{ mg}\cdot\text{L}^{-1}$  and  $\text{Cl}/\text{Br} = 740$ . These are long-turnover-time groundwater samples showing a remarkable contribution of endogenous chloride (Table 2).

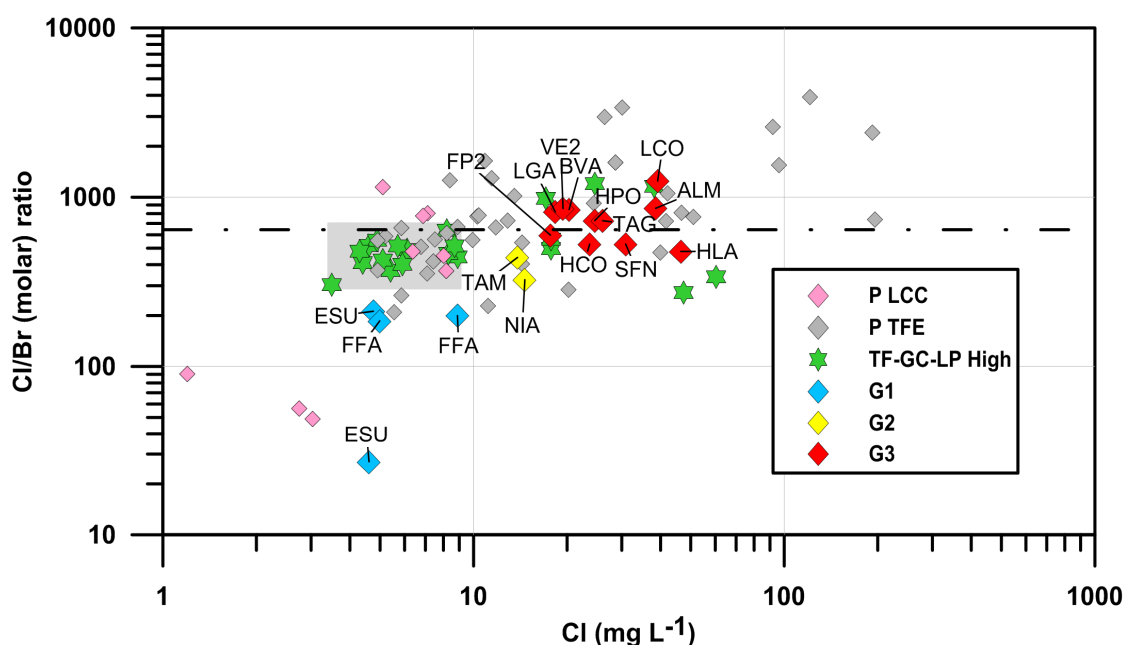
Average-weighted  $C_R$  and  $\text{Cl}/\text{Br}$  values increased from recharge to long-turnover-time groundwater (Table 2) due to (1) the combination of an increasing smoothing effect as the percolation time of recharge in transit increases in Group 1; and (2) the progressive contribution of endogenous chloride as the average turnover time of groundwater increases in Groups 2 and 3 (Table 2). The overall effect is shown by lower coefficients of variation of  $C_R$  and  $\text{Cl}/\text{Br}$  in Group 3 (Table 2).  $C_R$  and  $\text{Cl}/\text{Br}$  values are in agreement with findings reported in Tenerife Island by [21]. Group 1 was selected to calculate yearly recharge in the LCC recharge area by using  $C_R$  data from galleries ESU and FFA. Note that no-forced trends in  $C_R$  and flow dynamics were observed in galleries ESU and FFA (Figure 5). This is a prerequisite of steady conditions for recharge evaluations [9,50].



**Figure 5.** Temporal evolution of data in selected sampling points. (a)  $\text{Cl}/\text{Br}$  molar ratio; (b) Discharge flow ( $\text{L}\cdot\text{s}^{-1}$ ) in galleries and piezometric level (m a.s.l.) in S-1 and S-2 boreholes; and (c)  $C_R$  ( $\text{mg}\cdot\text{L}^{-1}$ ) in galleries and boreholes S-1 and S-2. Data source: [30,33], and CIATFE hydrochemical database in [33].

#### 4.4. Recharge Evaluation

In the LCC recharge area the Cl/Br ratio was 255 in atmospheric bulk deposition (Table 1) and 144 in recharge water (Table 2). As commented in Section 4.2, Br was only measured in three rainwater samples in collectors 9 and 21. Similar few Br data exist for recharge water [33]. This low statistical significance may be the reason of the negative bias of Cl/Br values, when compared with Cl/Br data ranging from 250 to 300 in high-elevation recharge waters in Tenerife Island reported by [21] (Figure 6). However, the small negative bias in Cl/Br values does not prevent the recharge evaluation based on the premise of an atmospheric origin of  $C_R$  for a proper CMB application.



**Figure 6.** Plot of Cl ( $\text{mg}\cdot\text{L}^{-1}$ ) vs. Cl/Br molar ratio from different groups of samples studied. G1, recharge water; G2, shallow groundwater; and G3, deep groundwater as in Table 2 [33]. Data from atmospheric bulk deposition samples in the LCC area (P LCC) and in other areas of Tenerife Island (P TFE) after [33]. Groundwater samples from high and mid-slopes areas (over 1000 m a.s.l.) in Tenerife (TF), Gran Canaria (GC), and La Palma (LP) Islands (TF-GC-LP High) after [21]. Cl/Br =  $655 \pm 4$  for global seawater (dashed line) and Cl/Br =  $484 \pm 93$  (20 samples) for recharge waters in high and mid-slope areas in TF, GC, and LP Islands (dashed grey square) were taken from [21].

Using average-weighted yearly  $C_P = 5.37 \text{ mg}\cdot\text{L}^{-1}$  (Table 1),  $C_R = 7.73 \text{ mg}\cdot\text{L}^{-1}$  (Table 2) and  $P = 914.7 \text{ mm}\cdot\text{year}^{-1}$  from AEMET weather stations into Equation (2), calculated yearly  $R$  in the LCC recharge area was  $631.1 \text{ mm}\cdot\text{year}^{-1}$  in year 2005–2006, *i.e.*, 69% of yearly  $P$ . Note that the recharge area elevation for selected galleries (Table 2) was similar to the elevation of open collectors for sampling bulk deposition (Table 1) and AEMET weather stations used for yearly  $P$ , thus allowing reliable comparisons of  $R$  and  $P$ .

## 5. Discussion

Las Cañadas Caldera (LCC) is a high-permeability endorheic basin favouring high recharge rates. The CMB method was used to estimate net aquifer recharge ( $R$ ) in the wet hydrological year 2005–2006. This year provides information on the maximum threshold of renewable groundwater resources expected at the area. Yearly  $R$  was  $631.1 \text{ mm} \cdot \text{year}^{-1}$ . The recharge-to-precipitation (hereafter  $R/P$ ) ratio was 0.69; note that the  $E/P$  ratio was 1.08 in this year (Figure 3e). This figure is in good agreement with the  $R/P$  ratio about 0.65 obtained for similar wetter years (Figure 3) through an independent lumped-parameter rainfall-runoff model operated by CIATFE [2,59] from hydrological years 1944–1945 to 2003–2004 [30]. The positive relative difference was about 0.04.

About the CIATFE model, it was programmed to evaluate water resources throughout Tenerife Island [2,59]. For this purpose (1) the island was discretized into a  $1 \text{ km} \times 1 \text{ km}$  grid; (2) in each grid node precipitation was measured or interpolated from existing 230 weather stations, evaporation and transpiration coefficients were calculated, and overland runoff was evaluated; (3) in each grid node, potential aquifer recharge is deduced as difference in precipitation, evapotranspiration, and runoff, taking the cumulative water surplus from high to lower grid-nodes into account; (4) piezometric records were used for calibration; and (5) daily estimates were added to get yearly values. In the LCC area, the CIATFE model provided an average  $R/P$  ratio about 0.68 for the 60-year modeling period, as deduced from average yearly precipitation of  $489 \text{ mm} \cdot \text{year}^{-1}$  and potential recharge of  $334 \text{ mm} \cdot \text{year}^{-1}$  [30].

A low divergence among potential recharge estimates obtained through accurate physical (e.g., soil water balances combined with hydrodynamic methods) and tracer (e.g., the CMB method) techniques was also documented in other geographical domains having similar high  $R/P$  ratios and variable contribution of diffuse and preferential recharge mechanisms [10,14,16]. The low relative difference between the CMB method and the CIATFE model is attributable to (1) homogeneity of the system response to recharge inputs; (2) negligible water losses by surface and interflow runoff induced by the particular LCC aquifer boundary; (3) accuracy of actual evapotranspiration estimated by the CIATFE model; (4) fast infiltration induced by the sparsely-vegetated condition of the area and the high permeability of the vadose zone, thus favoring reliable comparisons of average-weighted yearly  $C_P$  and  $C_R$ ; and (5) high representativeness of  $C_R$  data from galleries ESU and FFA. Galleries are proposed as optimal sampling points for potential recharge in transit through the vadose zone, a desirable condition in active volcanic areas in order to avoid the contribution of volcanogenic halides to groundwater. However, low divergence does not necessarily provide an additional confidence in both recharge estimates [12,60]; this is a necessary but not sufficient condition for confident results.

## 6. Conclusions

In view of the results, four conclusions arise: (1) potential recharge estimates deduced from sampling  $C_R$  in the vadose zone just above the water-table prove to be a reliable proxy of net aquifer recharge; (2) the apparent linearity in  $R/P$  ratios among the CMB method and the CIATFE rainfall-runoff model estimates allows for comparisons; (3) results provide groundwater resources around  $80.8 \text{ Mm}^3$  in the wet 2005–2006 hydrological year and  $42.8 \text{ Mm}^3$  in an average-rainfall period [30] taking the  $128 \text{ km}^2$  recharge area of LCC into account, thus contributing between 12% and

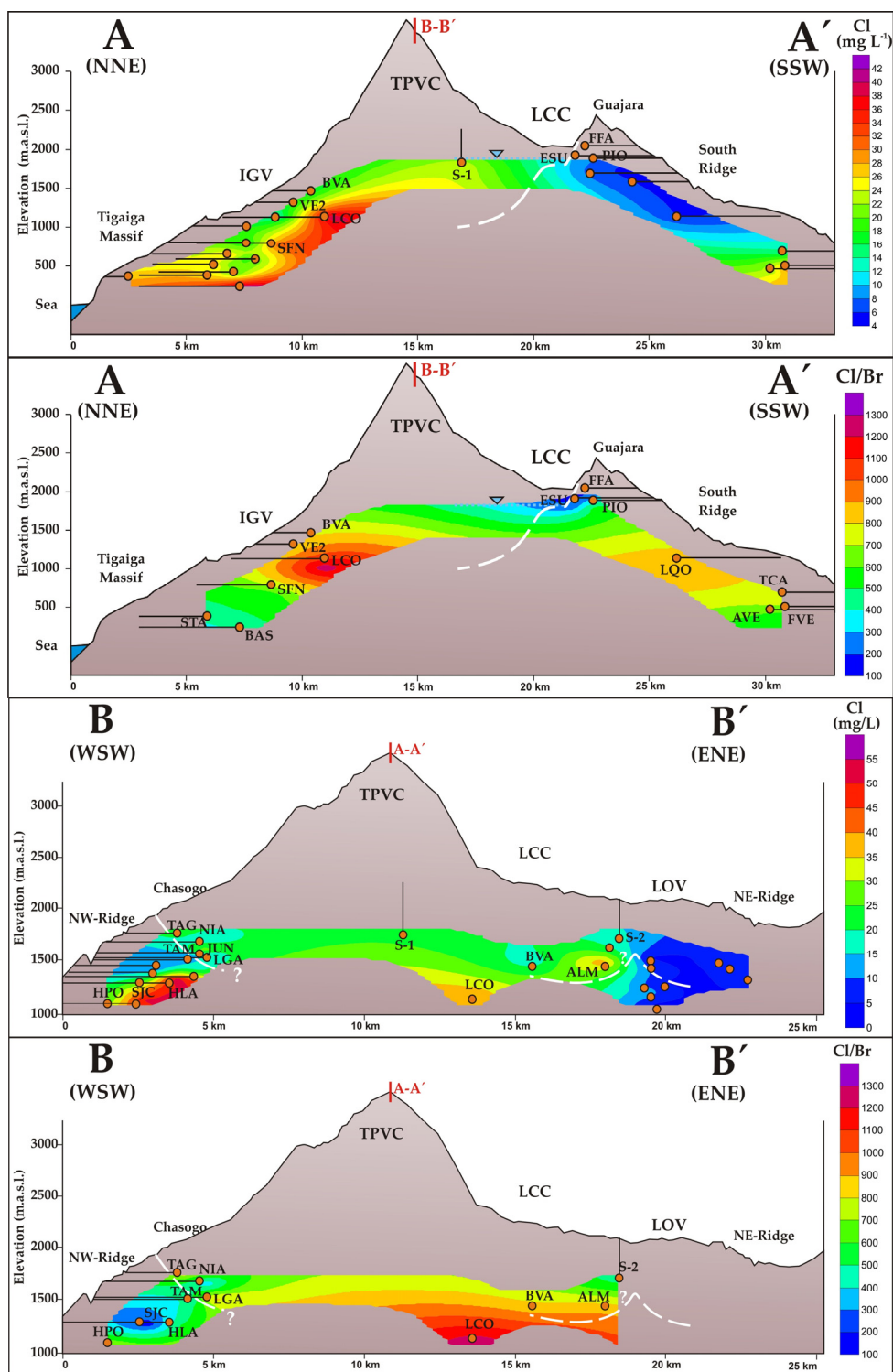
23% to the total 358 Mm<sup>3</sup> renewable groundwater resources estimated in Tenerife Island (2037 km<sup>2</sup>) through the CIATFE model [2]; and (4) longer data series of  $C_P$  and  $C_R$  are desirable to use the CMB method for long-term recharge evaluations and calibrations. This recharge evaluation allows for planning groundwater sustainability. In the LCC aquifer, average yearly discharge of 37.6 Mm<sup>3</sup> was recorded in galleries draining the LCC aquifer in the period 2002–2006 [33,44], thus the discharge-to-recharge ratio is 0.88 for an average hydrological period. The 0.12 difference is attributed to diffuse discharge to other aquifers.

In large areas of Tenerife Island, as well as in other active oceanic volcanic islands, the contribution of endogenous halides from the volcanic-hydrothermal system [39,41–43] to groundwater is the largest source of uncertainty to use the CMB method when groundwater samples are used for net aquifer recharge, irrespective of the recharge-to-precipitation ratio induced by local climate and soil properties. Permanent precipitation of halides in the vadose zone may occur by combination of two successive high-order controls (1) a testable degassing of endogenous halides through the vadose zone, as reported by [43] in Tenerife Island; and (2) low recharge-to-precipitation ratios such as reported in drylands [61], thus favoring temporary retentions. The second control is negligible in the LCC area. So the combined effect results in a negligible precipitation of endogenous halides in the vadose zone. Unfortunately, there is no vertical Cl/Br for assessing potential soil halide dissolution occurring.

In spite this constraint, LCC is a rare, suitable area to use the CMB method. The suitability of the CMB method is supported by two basic steady conditions (1) no-forced trends induced by pumping and climate were identified in  $C_R$  and flow dynamics in recharge sampling points (Figure 5); and (2) similar low Cl/Br ratios were found in atmospheric bulk deposition and recharge water (Figure 6) as prerequisite for asserting the atmospheric origin of  $C_R$  and discarding a relevant precipitation of endogenous halides in the vadose zone.

In Tenerife Island, the Cl/Br ratio in high and mid-slope recharge water vary in the 150–400 range, whereas the progressive HCl degassing in volcanic-hydrothermal systems can raise Cl/Br up to 1300 (Figures 6 and 7) as pointed by [21]. The Cl/Br values reported in this work are in good agreement with existing information in other active volcanic-hydrothermal systems [62,63]. This available Cl/Br database was of interest in the spatial identification and zoning of disadvantageous areas having preferential contribution of endogenous halides, thus limiting the CMB application.

This paper evaluates recharge dynamics in sparse-data areas in high-elevation volcanic oceanic islands. The paper contributes to enhance the applicability of the CMB method in hydrogeological systems where reported contributions of endogenous halides to groundwater are often a main cause to invalidate the application. The mapping of the Cl/Br ratio in groundwater in Tenerife Island (Figure 7) is a contribution of this paper with application for planning aquifer recharge studies and volcanic degassing monitoring in the future. Understanding recharge dynamics is key for groundwater resources management focussed in sustainable socioeconomic development in these isolated regions.



**Figure 7.** Distribution maps of (a) chloride content ( $\text{mg}\cdot\text{L}^{-1}$ ) and (b) Cl/Br ratio in groundwater in Tenerife Island (see location of cross-sections A-A' and B-B' in Figure 1a and Figure 4). Horizontal and vertical lines mean projected locations of galleries described in Table 2 and scientific boreholes S-1 and S-2, respectively (see location in Figure 4). Dashed blue line in cross-section A-A' is the water-table position. White line in cross-sections A-A' and B-B' represents the upper boundary of the basement, as inferred by [33].

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## Author Contributions

Rayco Marrero-Díaz and Francisco J. Alcalá conceived the subject of the article; Rayco Marrero-Díaz, Francisco J. Alcalá, Nemesio M. Pérez and Dina L. López designed the work; Rayco Marrero-Díaz and Germán D. Padilla collected data; Rayco Marrero-Díaz, Gladys V. Melián and Eleazar Padrón carried out laboratory measurements and analyzed the data; Rayco Marrero-Díaz, Francisco J. Alcalá and Dina L. López wrote the manuscript.

## Conflicts of Interest

The authors declare no conflict of interest.

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