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Article

Estimating Natural Recharge by Means of Chloride Mass Balance in a Volcanic Aquifer: Northeastern Gran Canaria (Canary Islands, Spain)

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Abstract: The chloride mass balance method was used to estimate the average diffuse groundwater recharge on northeastern Gran Canaria (Canary Islands), where the largest recharge to the volcanic island aquifer occurs. Rainwater was sampled monthly in ten rainwater collectors to determine the bulk deposition rate of chloride for the 2008–2014 period. Average chloride deposition decreases inwardly from more than 10 $g \cdot m^{-2} \cdot year^{-1}$ to about 4 $g \cdot m^{-2} \cdot year^{-1}$. The application of the chloride mass balance method resulted in an estimated average recharge of about 28 hm^3/year or 92 mm/year (24% of precipitation) in the study area after subtracting chloride loss with surface runoff. The average storm runoff was estimated to be 12 hm^3/year (9% of precipitation) for the 1980–2014 period. Runoff was sampled during scarce rainy periods, which produce surface water flow. Average recharge varies from less than a few mm/year near the coast up to 270 mm/year in the highlands (about 33% of average rainfall), with a close-to-linear increase inwardly of about 18 $mm \cdot year^{-1} \cdot km^{-1}$. Recharge rate uncertainty corresponds to an estimated CV of 0.3–0.4 because of the short data series available.

Keywords: recharge; volcanic aquifer; chloride mass balance; Gran Canaria Island

1. Introduction

Groundwater often forms a dominant part of the total water resources in many volcanic islands and may play a key role in local economic development. In many cases, intensive irrigated agriculture uses the largest fraction of available water resources, in concurrence with other water uses, which may be needed economically and socially as, for example, a source of employment. Accordingly, by taking into account water quantity and quality aspects, natural aquifer recharge evaluations are crucial for evaluating aquifer water resources and their management.

Recharge is a complex natural phenomenon and one of the most difficult hydrological variables to measure and/or estimate [1], considering the: unavoidable simplifications to calculate it; wide temporal and spatial variability; paucity of observations; gaps in data series; and lack of measurements of the hydraulic parameters needed to apply recharge calculation codes and models. All this explains the commonly large uncertainty of the results. Several approaches have been developed to quantify groundwater recharge from precipitation, such as direct measurement, water-balance methods, and tracer techniques [2–5]. In order to improve recharge estimations, combining different techniques that are as independent as possible from each other is advisable [6–9]. The detailed application of many of these methods is costly and time consuming, and a long monitoring time is needed to obtain reliable results when direct methods are used [2]. For this reason, natural tracer techniques based on environmental components are widely and successfully used.

Regional recharge is one of the most difficult hydrological components of the water balance to estimate [10], especially in aquifers where rock fracturing plays a key role, which is the case of volcanic terrains [11]. This is compounded by adequate water table data records and accurate outflow measurements or evaluations not being available to calibrate water-balance models. This is a frequent circumstance in volcanic islands due to a regularly profound water table depth, and also to the fact that groundwater outflow is produced in large water bodies, such as the sea.

For realistic and sound groundwater management and planning, recharge estimates have to be accompanied by an estimation of uncertainty, which is often significant. This estimation derives from error propagation analyses supported by sensitivity analyses to obtain weighting coefficients.

The chloride mass balance (CMB) method of atmospheric bulk deposition is the most widely used tracer technique to estimate long-term groundwater recharge under steady-state conditions [6]. It has been applied in many studies worldwide [12–15]. Knowledge of atmospheric chloride deposition is a prerequisite for applying this method, which is never straightforward given a range of processes that control atmospheric deposition [16–19] as they fluctuate temporally and are spatially variable, which makes extrapolating point measurements difficult. This has often been recognized as the main source of uncertainty when applying the CMB method [6,15,20,21], along with the right evaluation of the chloride concentration of recharge water [5]. Long-term average CMB data taken at different points are necessary to estimate long-term average recharge values. Long-term records of CMB variables are rare, so they have to be estimated from available short-term records, which are often only 1–5 years long. This period is shorter than the minimum 10-year period required to minimize uncertainty, especially for atmospheric chloride deposition [15,19], although this uncertainty is still intrinsically significant. Short-term records may not adequately represent long-term values, and may increase the uncertainty of recharge evaluation.

Knowledge of the tracer concentration in recharge water is just as important as average deposition. By assuming that tracer transport through the unsaturated zone is conservative, which it is for chloride, and under steady-state conditions, the tracer concentration at the upper part of a saturated zone can be used as a good proxy of recharge water concentration, provided that recharge is active enough to safely neglect any diffusion effects from below. This is not the case in arid areas, especially if the water table is deep, as diffusion effects are strong; in particular, recharge water from old periods may be in transit. Since the tracer concentration in the groundwater from springs and deeply penetrating wells is a mixture of locally recharged water and groundwater upflow [5], corrections need to be made to the tracer concentration in recharge water. Adequate proxy selection significantly contributes to uncertainty.

On the Canary Islands, the CMB method to evaluate recharge, in addition to the case presented herein for the northeastern Gran Canaria Island, has been successfully applied in:

(1) Betancuria Massif, on the Fuerteventura Island, under arid conditions; average recharge was calculated from four open rainwater collectors in operation for 422 days and the calculated average recharge ranged from 9 to 33 mm/year (90% to 27% of precipitation) [22] with quite a large uncertainty;

(2) Las Cañadas aquifer, on the central Tenerife Island, when five rain collection stations were in operation in hydrologic year 2005–2006; the average recharge was estimated to be 215 mm/year (44% of precipitation) [23];

(3) La Aldea aquifer [24], under semiarid conditions;

(4) on La Gomera Island with a detailed groundwater chloride map, corrections were applied for mixing due to slope effects and after assuming deposition rates that had been extrapolated from other islands [5];

(5) the Amurga Fonolitic Massif on the southeastern part of Gran Canaria Island using chloride deposition [25] and ^{13}C-corrected ^{14}C data in a sloping aquifer to obtain the average recharge rate. This resulted in an areal average of about 4 mm/year, from less than 1 mm/year on the coast to 12 mm/year at the top of the wedge-shaped massif [5]. In all these cases, the recharge process was assumed to be under steady-state conditions, even in arid areas, provided that no contribution from deep-seated formations took place.

This paper presents the estimated groundwater average recharge on the northeastern Gran Canaria Island (Canary Islands, Spain) by means of the atmospheric chloride mass balance method, and also its uncertainty. This area is considered the main recharge area of the island given its heavier rainfall, lower temperature and favorable soil conditions.

2. Study Area

The Canary Islands, in the northeastern Central Atlantic Ocean close to the African continent, comprise seven main islands and several islets (Figure 1). The archipelago is in the Saharan dry belt, with regional rainfall averaging 70–150 mm/year, which is the case of the eastern islands. Nevertheless, rainfall depends on the island altitude effect on their north faces, where humid trade winds are intersected and pushed upward. Thus rainfall increases orographically and reaches average values of up to 1000 mm/year.

Gran Canaria, located in the central part of the archipelago, is almost coned-shaped, with a diameter of 50 km and a maximum elevation of 1949 m a.s.l. (above sea level). It is dissected by deep radial gullies.
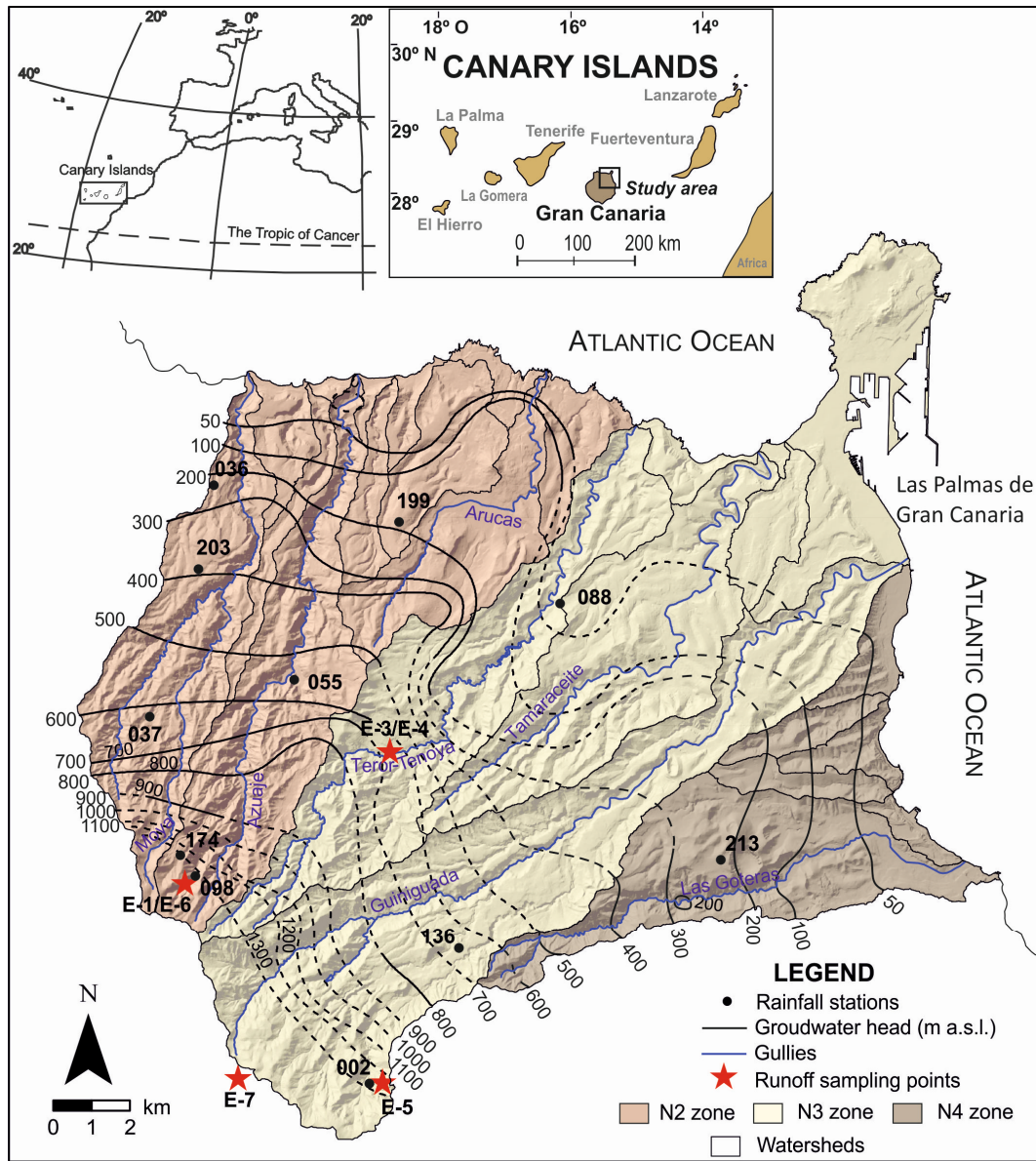

Figure 1. Study area, location of rainfall stations, where samples were collected, and runoff sampling points. Groundwater head contours (2008–2009), modified from [26,27].

The island aquifer is conceptualized as a single, stratified heterogeneous water body, with groundwater flowing from recharge areas at high altitude in the central part of island toward the coast. Natural discharge is produced along the coast, which took place through springs at gully bottoms in the past, but currently occurs by means of wells and water galleries. Groundwater is recharged and flows through different rock formations on the island, which are hydraulically connected and actually form a single, but heterogeneous, island aquifer system [28]. There are some exceptions, such as the La Aldea aquifer in the western part of the island, which is hydrogeologically isolated from the rest of the island [29] and only receives surface water inflow from three storage reservoirs upstream through a deep narrow canyon.

The northeastern area of the Gran Canaria Island considered herein covers 312 km^2 of surface area, and includes areas N3 and N4 and part of area N2 of the hydrological zoning of Gran Canaria (Figure 1). The study area limits are the sea and the watershed divides of the major gullies.

The study area is considered the most favorable one for groundwater recharge on the island due to the relatively high rainfall, the high steep relief that intercepts prevailing trade winds, the young permeable materials on the surface, low water retention soils and moderate-density vegetation. Climate varies from the coast to the highlands, with conspicuous changes in temperature and rainfall. The annual average temperature ranges from 14 °C in the highlands to 21 °C on the coast, with an average value of 18 °C. Weighted average rainfall (1980–2014) is about 490 mm/year, and exceeds 750 mm/year in wet years, and remains below 200 mm/year in dry years. Rainfall increases with altitude, and ranges from an average annual rainfall (1980–2014) of 250 mm/year near the coast to 750 mm/year in the highlands, and close to 900 mm/year locally.

In the study area, groundwater follows the insular pattern that flows radially from summit to coast (Figure 1). The water table varies from a depth of 137 m in coastal areas to 200 m in the middle and high areas on interfluve flats. Groundwater flows predominantly through the Pliocene basanitic lava flows and ignimbrites (Roque Nublo group), and the Miocene trachytic and phonolitic pyroclastic deposits and lava flows. Recharge is mainly the result of rainfall, but some irrigation return flows from the banana crop areas and contributes to this recharge on the coastal fringe.

3. Materials and Methods

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

The chloride mass balance method compares total chloride deposition (wet and dry) on the land surface with chloride concentrations in groundwater. It is assumed that chloride is a conservative ion, and that the only chloride (Cl) source is atmospheric deposition through rainwater (wet deposition) and aerosols and dust (dry deposition). Their addition is bulk deposition. Under long-term steady-state conditions of atmospheric deposition, given the evapoconcentration (concentration of salts in water due to evaporation and plant transpiration) in soil, and flow through the unsaturated zone profile—These being the expected conditions in the study area—Groundwater receives an average mass flow that matches the contribution made by average atmospheric deposition, minus the average output produced by direct runoff [3,5,20,30]. In other circumstances, corrections have to be made or the method cannot be applied.

The basic equation for quantifying recharge using the CMB method is:

$$R \cdot Cl_R = D_P - E \cdot Cl_E \tag{1}$$

where R is recharge, E is runoff, D_P is total atmospheric chloride deposition (subindex P refers to precipitation), and Cl_R and Cl_E are the chloride concentrations of recharge and runoff, respectively. The equation refers to the total monitoring period, or divided by the length of the time period to the rates. D_P is obtained from the accumulation of the successive depositions that correspond to each sampling period. If *i* is one of the sampling periods of a total of n periods, the total deposition rate can be calculated as:

$$D_P = \frac{1}{d} \sum_{i=1}^{n} Cl_{Pi} \cdot P_i \tag{2}$$

where Cl_P = chloride concentration in the water collected during the sampling period (mg·L^{-1}); P = precipitation during the sampling period (mm/year); $d = \sum_{i=1}^{n} d_i$ total number of days for n sampling periods; to avoid seasonal effects as much as possible, d should comprise a number of complete years.

A discussion of the variables in Equations (1) and (2) is provided in [15,20].

3.2. Rainwater Sampling

In order to determine the total chloride deposition in rainfall, precipitation samples were collected from 10 rainwater open collectors located at different altitudes (Figure 1) for 2008–2014 or for 2010–2014, depending on the collectors (Table 1).

Table 1. Rainfall sampling stations' designation and sampling period. *n* = number of samples.

Station	Sampling Period		*n*
036	6 November 2008	5 November 2014	48
037	31 October 2008	5 November 2014	52
055	30 October 2008	5 November 2014	54
098 *	31 August 2010	5 November 2014	36
174 *	31 October 2008	1 July 2010	18
203	31 October 2008	5 November 2014	52
002	4 February 2010	4 November 2014	37
088	4 February 2010	4 November 2014	30
136	4 February 2010	4 November 2014	35
199	4 February 2010	4 November 2014	30
213	4 March 2010	4 November 2014	41

Note: * Stations 174 and 098 are considered the same because the collector was moved to a nearby location in July 2010.

Collectors were placed close to existing rainfall stations, which belong to the Gran Canaria Water Council, where daily precipitation data were measured. A floating paraffin-oil layer was added to the collector pot to avoid evaporation. Samples were collected monthly or after dry months, which usually coincided with summer, over a longer period, which was needed to obtain a sufficient water volume for the chemical analyses.

3.3. Runoff Water

No permanent surface runoff exists on Gran Canaria Island. It occurs sporadically and is associated with short, heavy storms. Surface runoff is produced mainly in highland areas where the larger amount of precipitation is recorded, and is retained and stored in the reservoirs located in high and middle areas. Surface runoff is scarce, or even null, in coastal areas. Runoff gauging stations do not exist.

Runoff has been calculated by applying the curve-number method of the US Soil Conservation Service [31,32] for the 1980–2014 period [33]. This is an empirical method to estimate the runoff

produced by storms in a watershed according to precipitation by taking into account current water storage in the soil of the basin as a result of rainfall infiltration. A geographical information system (GIS) allowed the discretization of the area in different zones according to slope, soil use and soil typology. By overlapping these factors, a map of approximately the uniform areas was produced, which was suitable to estimate runoff by rainfall storms in the different zones of the study area, as well as the runoff coefficient (runoff/precipitation). Using the data from three reservoirs located in the area, a validation attempt was made with good results ($R^2 > 0.75$). However, as the reservoirs are located in the high part, it was not possible to reliably apply the results to the remaining area. The runoff estimation results are shown in Figure 2.
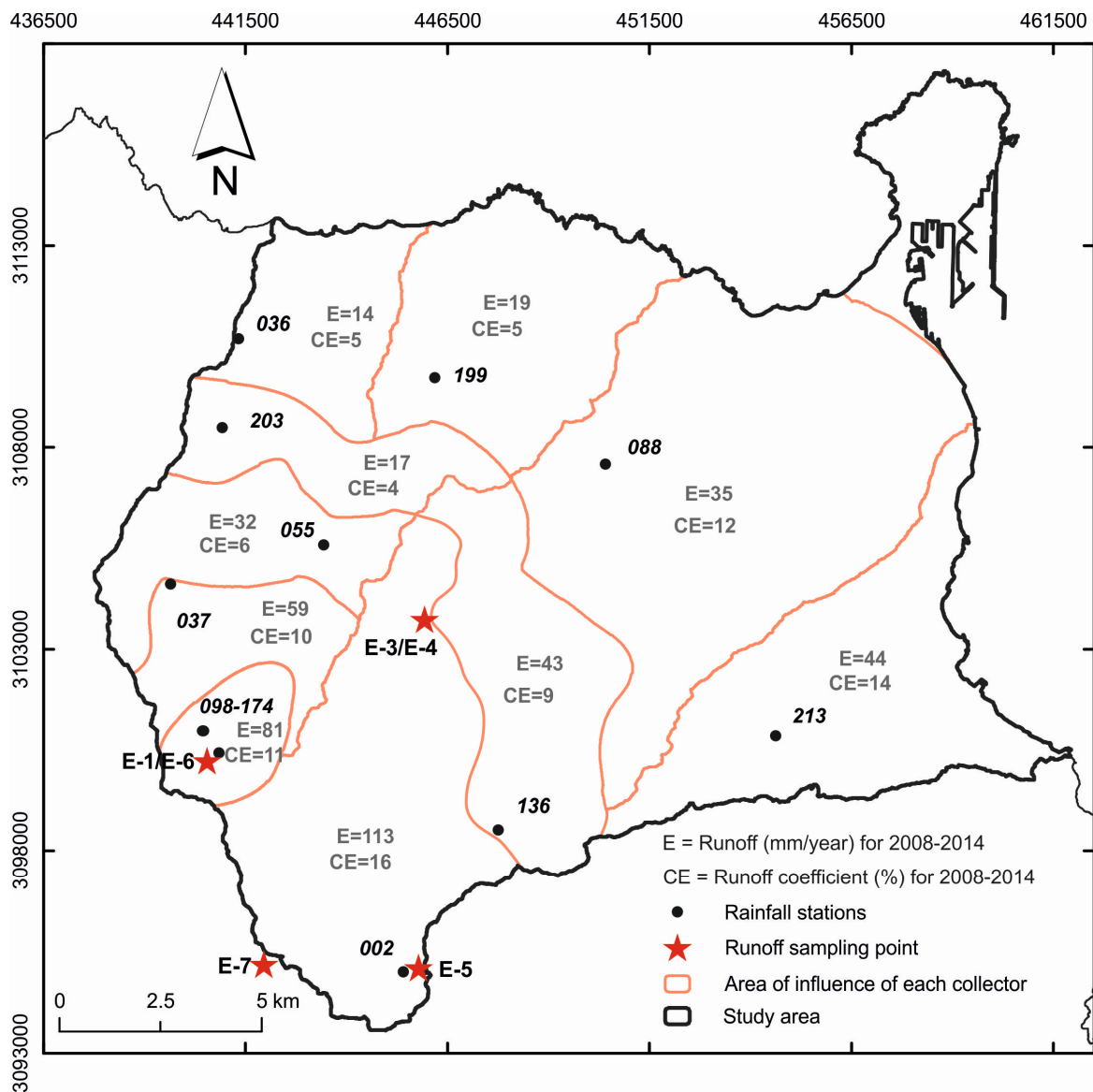

Figure 2. Area of influence of each collector and spatial distribution of the estimated runoff and runoff coefficients for 2008–2014, modified from [33]. **Bold**-*italic* numbers correspond to the rain-gauge station code (rain collectors).

Due to the droughts in 2011–2012 and 2012–2013 hydrologic years, and also to the surface runoff behavior noted in the aforementioned study area, only six surface runoff water samples were collected

in four different locations in different gullies (Figure 1). Three of these samples were collected during the same storm that took place in February 2013.

3.4. Recharge Water (Groundwater)

In order to obtain an approach to the chloride concentration of recharge water in the different study areas shown in Figure 2, a map of chloride iso-concentration lines was devised with the data from a field campaign done in 1997 by the Island Water Authority. Samples with >10 mg/L of nitrate are assumed to be affected by irrigation return flows or by other recharge sources, and were consequently eliminated. This map was supplemented with data from 32 springs and galleries sampled during the 2008–2012 period, which were highly coherent with previous data. The intention of this map is to compensate for scarce permanent springs, most of which lie in the highlands. Some bias is expected given the mixing from the up-slope recharge (slope effect), especially from wells. However, in this case, most of them are large-diameter shaft-wells with a relatively small penetration into the saturated zone in which groundwater caption takes place by means of horizontal boreholes at the well bottom.

4. Results

4.1. Chloride Concentration of Rainfall

Rainfall chemistry varies conspicuously in space and time. Figure 3 shows the modified Stiff diagrams of the representative rainwater for each rainfall station, weighted by the amount of rainfall in each collector for the whole study period. Rainwater is mainly of the sodium-chloride type. Salinity increases from highlands to the coast, which is characteristic of coastal areas with a great relief and a major wind component from the coast. The rainwater chemical composition depends also on the relative location of the collector: in the bottom of gullies or in divides; on the leeward side or the windward side. Concentrations are generally higher at lower altitudes and correspond to drier periods (March to October).

Table 2 offers the average precipitation and atmospheric chloride bulk deposition for rainwater, which are used to estimate recharge at each rainfall station site.

The average atmospheric chloride deposition in each collector during the sampling period (October 2008 to November 2014) ranged from 4.2 $g \cdot m^{-2} \cdot year^{-1}$ in collector 002 at an altitude of 1365 m a.s.l., where the highest rainfall and the lowest dry deposition were recorded, to 9.2 $g \cdot m^{-2} \cdot year^{-1}$ at 443 m a.s.l.

4.2. Runoff Chloride Concentrations

Runoff water is of the $Na-Mg-HCO_3-Cl$ type (Figure 3). It presented a significant chemical difference with rainwater due to a water-rock interaction in soil.

It was not possible to collect a runoff sample in all the areas where the rainfall collectors were located. So the chloride concentration in these stations was estimated from a regression line ($R^2 = 0.91$) obtained between the altitude and chloride concentration of the available samples (Figure 4). The estimated chloride concentration values and the average runoff estimated with the curve-number method for the area of influence of each rainfall station are shown in Table 3.
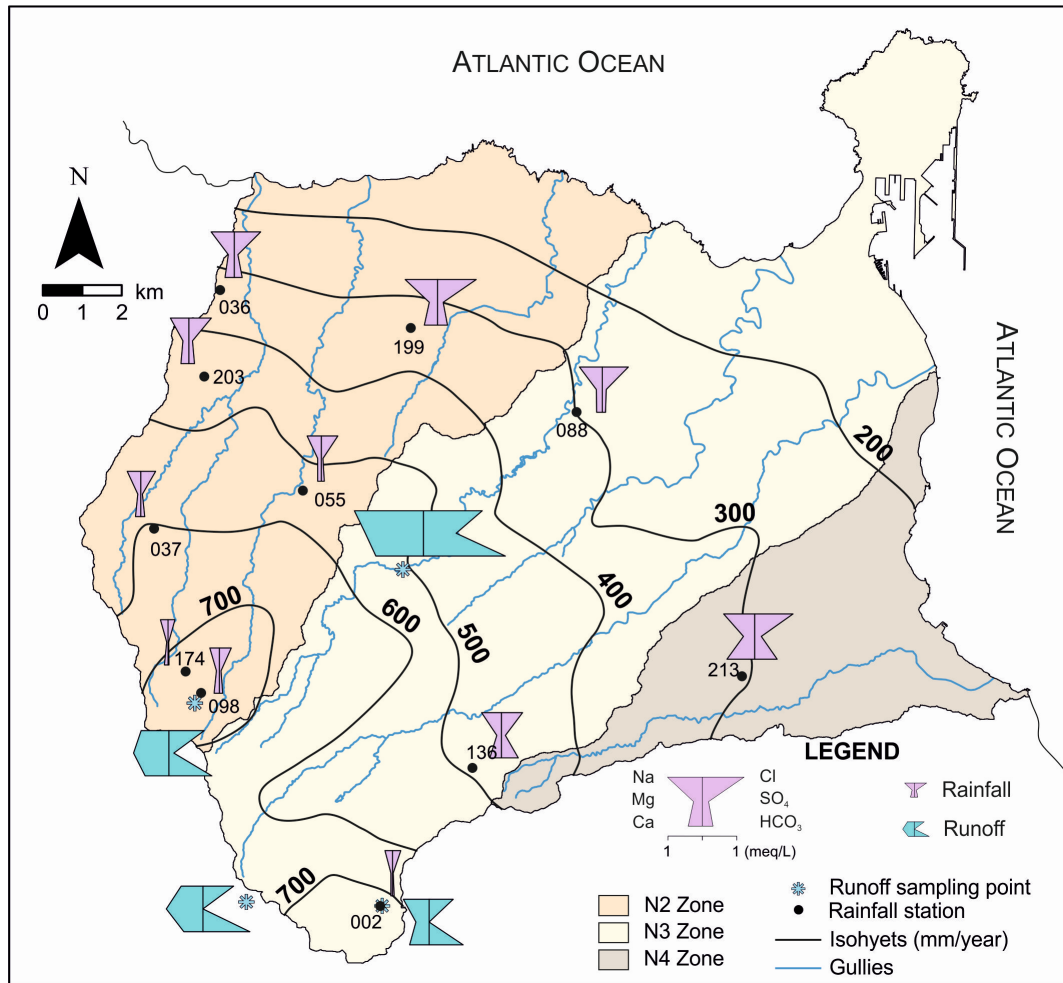
Figure 3. Modified Stiff diagrams of the representative rainwater chemistry of each rainfall station, weighted by the amount of rainfall in each collector. Runoff chemistry is also represented (average values when more than one sample was available at the same sampling point). Average isohyets (mm/year) for the 1970–2011 period are also shown.

Table 2. Results of atmospheric chloride bulk deposition in the area. Z = elevation; P = precipitation; C_P = precipitation-weighted average chloride concentration in rainfall during the study period; D_P = average atmospheric chloride deposition during the study period.

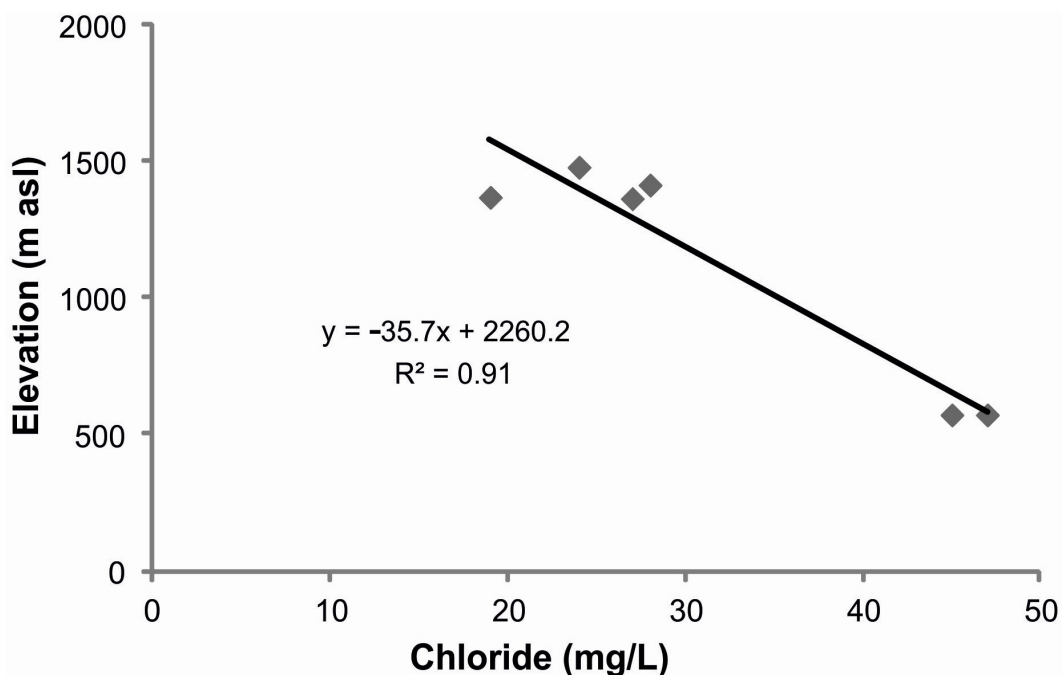| Zone	Station	Z m a.s.l.	P mm/year	C_P mg/L	D_P g·m^{-2}·year^{-1}
N2	036	375	264	21.9	5.3
	199	443	361	28.9	9.2
	055	577	581	12.9	8.8
	203	645	467	16.9	8.4
	037	990	598	11.9	7.1
	098-174	1370	739	7.8	6.0
N3	088	315	296	20.6	5.9
	136	841	491	18.2	7.5
	002	1365	715	6.7	4.2
N4	213	485	310	28.9	9.0

Figure 4. Chloride concentration in runoff samples *vs.* elevation.

Table 3. Average runoff for the 2008–2014 period, estimated by the curve-number method, and the chloride concentration, obtained by estimating the runoff mass flow for the area of influence of each rainwater station.

Station	Z (m a.s.l.)	Gully	Runoff (mm/year)	Chloride in Runoff (mg/L)
002	1365	Guiniguada	113	21
036	375	Moya	14	46
037	990	Moya	59	36
055	577	Azuaje	32	46
088	315	Teror	35	46
098	1370	Azuaje	81	27
136	841	Guiniguada	43	40
199	443	Arucas	19	51
203	645	Moya	17	45
213	485	Las Goteras	44	46

4.3. Chloride Concentration in Recharge Water

Groundwater showed highly variable salinity, as reflected by electrical conductivity (EC) within the 110–5000 μS/cm range after the 1997 data. The lowest Cl concentration (10 mg/L) was found in the mountain highlands, where most recharge was produced. The Cl concentration increased along the groundwater flow up to more than 1200 mg/L (Figure 5) as aridity enhanced the evapo-concentration of rain, which increased toward the coast. The chloride concentration in recharge water (Table 4) was obtained from Figure 5 at each collector location.
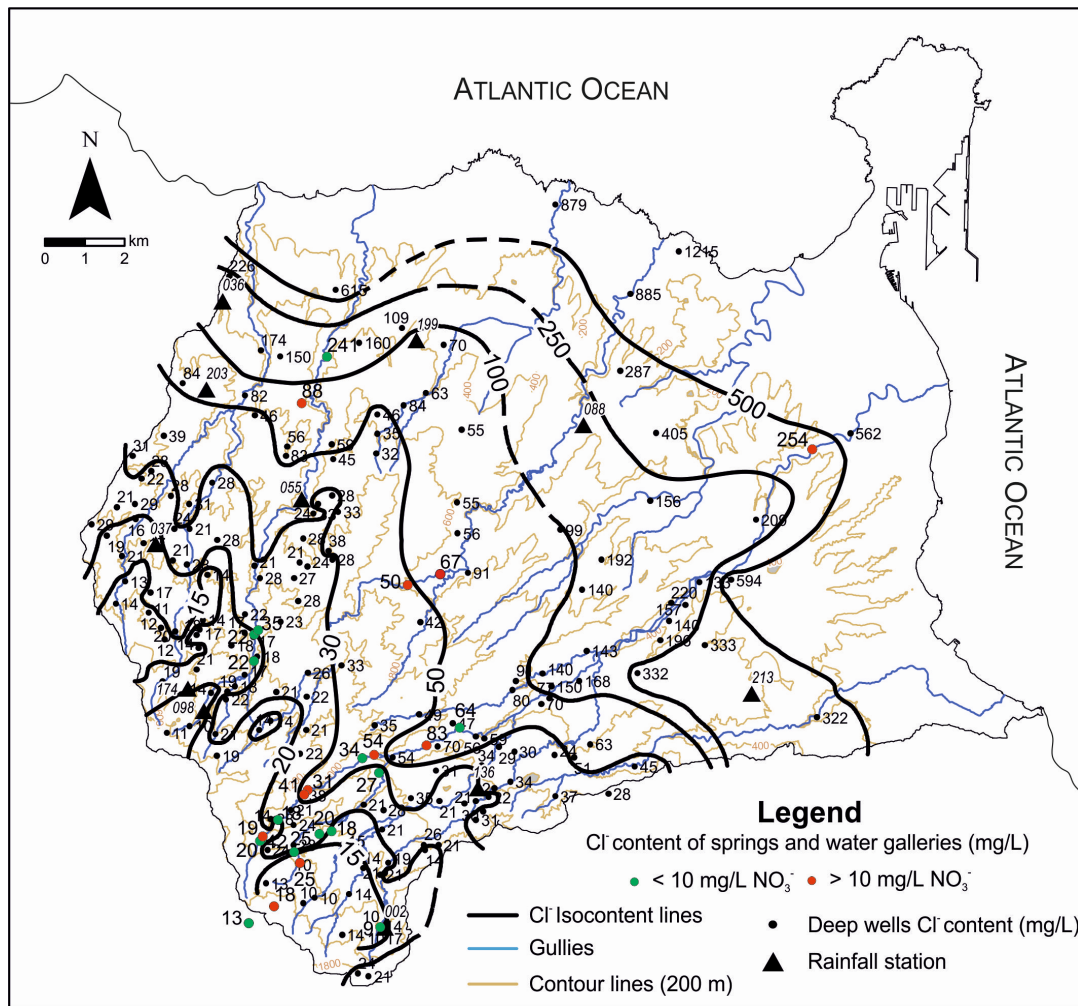
Figure 5. Chloride concentration (mg/L) isoline map in groundwater in 1997 using the data provided by the Water Council of Gran Canaria and the new data from the springs and galleries sampled in 2013.

Table 4. Average recharge estimated by the chloride mass balance method in each collector. Z = elevation; S = area of influence per collector; D_P = average deposition of atmospheric chloride during the study period; E = surface runoff; C_R = chloride concentration in recharge water (groundwater); C_E = chloride concentration in surface runoff water; R = estimated recharge; P = precipitation.

Zone	Station	Z m a.s.l.	S (km²)	D_P g·m⁻²·year⁻¹	C_R mg/L	$E·C_E$ (g·m⁻²·year⁻¹)	R mm/year	% R/P
N2	036	375	17	5.3	150	0.6	31	12
	199	443	33	9.2	75	1.0	109	30
	055	577	19	8.8	35	1.5	209	36
	203	645	15	8.4	60	0.8	127	27
	037	990	13	7.1	25	2.0	203	34
	098-174	1370	8	6.0	15	1.9	271	37
N3	088	315	77	5.9	200	1.7	21	7
	136	841	28	7.5	35	1.4	173	35
	002	1365	48	4.2	15	1.7	169	24
N4	213	485	41	9.0	300	2.1	23	8

Historical data were analyzed in wells with the data from different years to ensure that the chloride concentration was relatively constant and did not correspond to different sources that could change with time. The coefficient of variation of the chloride concentrations in several wells varied between 0.2 and 0.3.

4.4. Recharge Estimation

Recharge was estimated for each rainfall collector and was extrapolated to the entire study area after considering its area of influence. The estimated recharge results for each rainfall collector are shown in Table 4. The average recharge rates estimated for each collector ranged between 7% and 37% of average precipitation. Spatial distribution depended on the altitude and catchment where the rainfall collector was located.

Table 5 shows the extrapolation of the rainfall stations data to the whole area after considering the zones of the island's water plan. Extrapolation was carried out by considering the area of influence of each collector (Figure 2), isohyet distribution (Figure 3) and catchment limits. The catchment was divided into: Low, below the 400 mm/year isohyet line; Middle, between isohyets lines 400 and 600 mm/year; High, above the 600 mm/year isohyet line.

Table 5. Average annual precipitation (period 1970–2014) and long-term average annual estimated recharge obtained by the chloride mass balance method (2008–2014). S = surface of the respective areas. P_{total} refers to precipitation over the whole area.

Zone	Area	S (km²)	Precipitation		Recharge		%R/Ptotal
			mm/year	hm³/year	mm/year	hm³/year	
N2	Low	50	243	12.1	58	2.9	2.5
	Middle	34	530	17.9	172	5.8	5.0
	High	22	652	14.1	229	5.0	4.3
	Total:	**105**		**44.1**		**13.7**	**11.8**
N3	Low	77	234	18.1	17	1.3	1.1
	Middle	48	518	25	153	7.4	6.4
	High	26	661	17.0	157	4.0	3.5
	Total:	**151**		**60.1**		**12.7**	**11.0**
N4	Low	41	259	10.5	20	0.8	0.7
	Middle	2	491	1.1	173	0.4	0.3
	Total:	**43**		**11.5**		**1.2**	**1.0**
TOTAL		**299**	**387**	**115.7**	**92.1**	**27.6**	**23.8**

The highest precipitation rates in the study area were produced in hydrological zone N2 (Figure 1). This zone is more humid than the others because of the frequent "sea of clouds" caused by the orographic upheaval of trade winds against the northern face of Gran Canaria, which causes air moisture condensation. Recharge in this area was also the highest, 12% of total precipitation in the whole area. Recharge in the more arid (less exposed to trade winds) zone N4 was only 1% of total precipitation (Figure 1).

4.5. Uncertainty of Recharge

For normally distributed variables X, characterized by their mean $\bar{X}_\iota$ value and standard deviation S_{X_i}, the error propagation rule for function $X = f(X_i)$ is:

$$S_X^2 = \sum (\partial f(X_i)/\partial X_i)^2 S_{X_i}^2 \qquad (3)$$

If surface runoff is assumed negligible, Equation (1) lowers to $\bar{R} = \bar{D}/\bar{C}$ ($\bar{R}$ = average recharge; $\bar{D}$ = average atmospheric chloride deposition; $\bar{C}$ = average chloride concentration in local recharge). The error can be given by the coefficient of variation (CV, standard deviation divided by the mean). Equation (3) becomes $CV_R^2 = CV_D^2 + CV_C^2$. This can be easily extended to take into account surface runoff. The reader can do this readily. This extension has been considered in the calculations.

In the study area, the values of the standard deviations (S) are still poorly known due to the short monitoring period. Local data show a relatively slight variability of total deposition due to the significant contribution of the more stable dry deposition.

The analysis of data series from mainland Spain (Iberian Peninsula) indicated an expected average coefficient of variation for 4−6-yearlong measurement periods of chloride deposition D of $CV_D = 0.20$ with $CV_{CVD} = 0.5$ [15,20], which seems to agree with local data. The repeated chemical analyses for some springs and wells in the Water Authority files, and still unpublished data from Pilar Hernández's dissertation, indicate $CV_C = 0.2$ to 0.3 for chloride concentration as a proxy of the recharge water chloride concentration. Therefore, the average coefficient of variation of estimated recharge is about $CV_R = 0.3$ to 0.4.

5. Discussion

As shown in Figure 6, chloride contribution to precipitation is strongly influenced by distance from the sea. The detailed consideration of the results from each rainfall collector is complex as the different local circumstances have to be considered, some of which are still to be analyzed. Hence only general trends were considered herein. The highest values corresponded to the samples located near the coast given the incorporation of dust and chloride dry deposition from the marine aerosol. The bulk chloride deposition values obtained in this study were similar to the results obtained in previous studies conducted in Gran Canaria: between 4 and 5 $g \cdot m^{-2} \cdot year^{-1}$ in highland areas and up to 20 $g \cdot m^{-2} \cdot year^{-1}$ in coastal areas [24,25,34]. Atmospheric chloride deposition and other solutes play an important role in the climatic salinization of groundwater through evapoconcentration, especially when R/P is low (arid zones), which is the case for the Fuerteventura Island [22] and southern areas of the Gran Canaria Island. Precipitation increased linearly by 40 $mm \cdot year^{-1} \cdot km^{-1}$ and recharge by 18 $mm \cdot year^{-1} \cdot km^{-1}$, while deposition exhibited a poorly defined decreasing trend of about −0.3 $g \cdot m^{-2} \cdot year^{-1} \cdot km^{-1}$ (dry deposition decreased faster than rainfall increased). Consequently, the chloride concentration in rainfall decreased nonlinearly with distance to the coast.

The recharge rates estimated for each rain collector varied according to their location, orientation and rainfall recorded. The highest values correspond to the collectors located at medium and high altitude, and were generally higher in zone N2, dominantly oriented northerly, and the lowest in N4, dominantly oriented easterly.
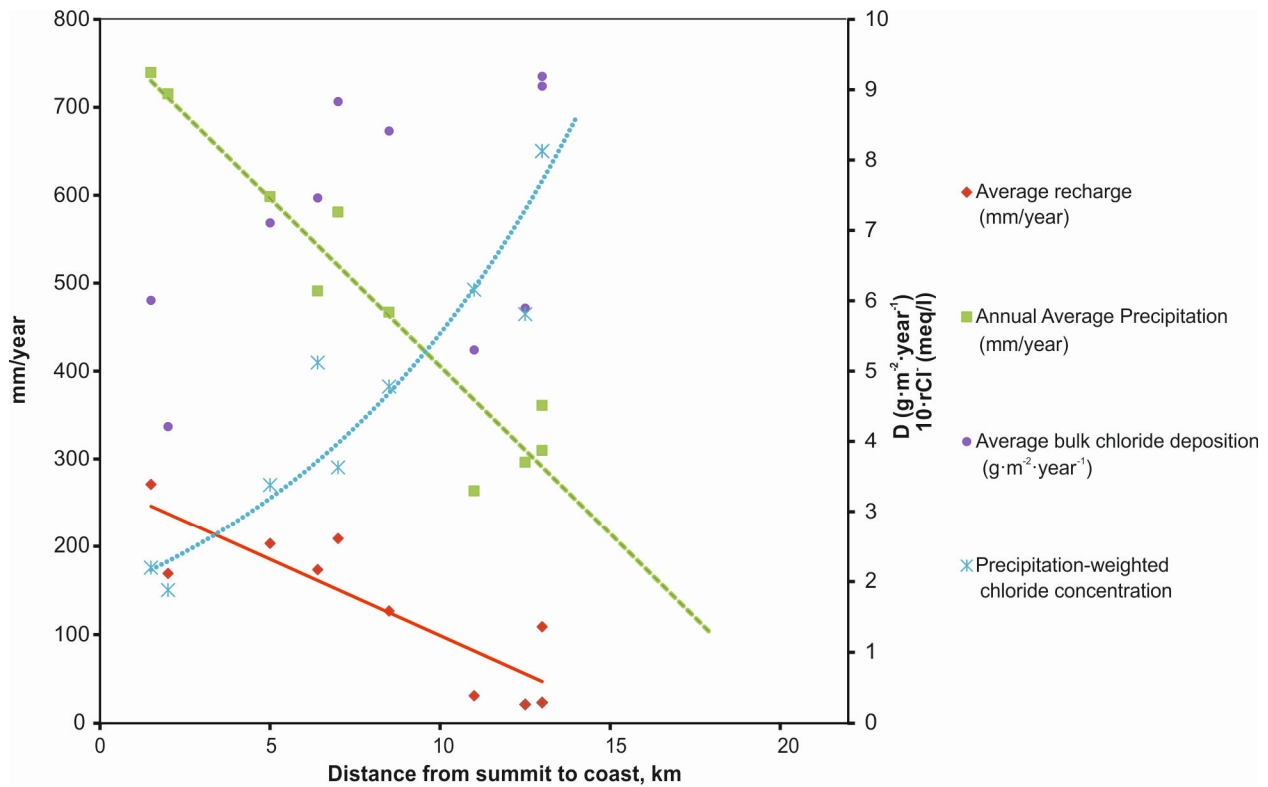
Figure 6. Long-term average recharge, annual average precipitation (period 1970–2014), average bulk chloride deposition and precipitation-weighted chloride concentration of rainwater *vs.* distance to the coast during the study period.

The estimated groundwater recharge in the considered areas is presented in Figure 7. About 80% of recharge was produced in high and middle zones. When runoff was taken into account, the estimated average recharge volume for the total study area was about 28 hm^3/year (92 mm/year), which was almost 24% of annual average precipitation. Should runoff be considered negligible [35], total average recharge would result in 34 hm^3/year (142 mm/year), approximately 30% of precipitation, which would be an overvaluation of about 18%.

In order to understand the relationships between the runoff chloride concentration and the estimated recharge, a sensitivity analysis was carried out by assuming the chloride concentration in runoff to equal, double and triple the rainfall chloride concentration. The results show that recharge varies between 11% and 22% of that obtained when considering runoff samples, and its extrapolation where it was not possible to obtain a runoff sample. Therefore, recharge is sensitive to changes in the chloride concentration in runoff.

The assumption that chloride concentration is related to altitude is supported by the fact that the salt concentration of the rainfall which produces runoff increases nearer to coastal areas due to the combination of an increased airborne marine influence and the aridity effect. After taking this into account, we considered that the error in the recharge calculation due to the runoff chloride concentration estimation, as previously done, is slighter than considering negligible runoff chloride exportation.

The recharge estimates obtained by the chloride mass balance method considered recharge due to precipitation, but not recharge by runoff infiltration along the gullies bed. Some approaches developed during the SPA-15 Project [33] indicate values of 1.2% of the precipitation infiltrated from runoff in

the gullies in hydrological area N3 (Figure 1), around 0.7 hm^3/year. These estimations were made by the difference among the income runoff in upper parts of catchments, the estimated direct runoff produced in catchments and measurements of runoff entering the sea. This value is negligible compared to the total recharge in the area of 13 hm^3/year. Moreover, much surface runoff is actually retained by the more than 20 reservoirs in the study area, whose leakage is minor.
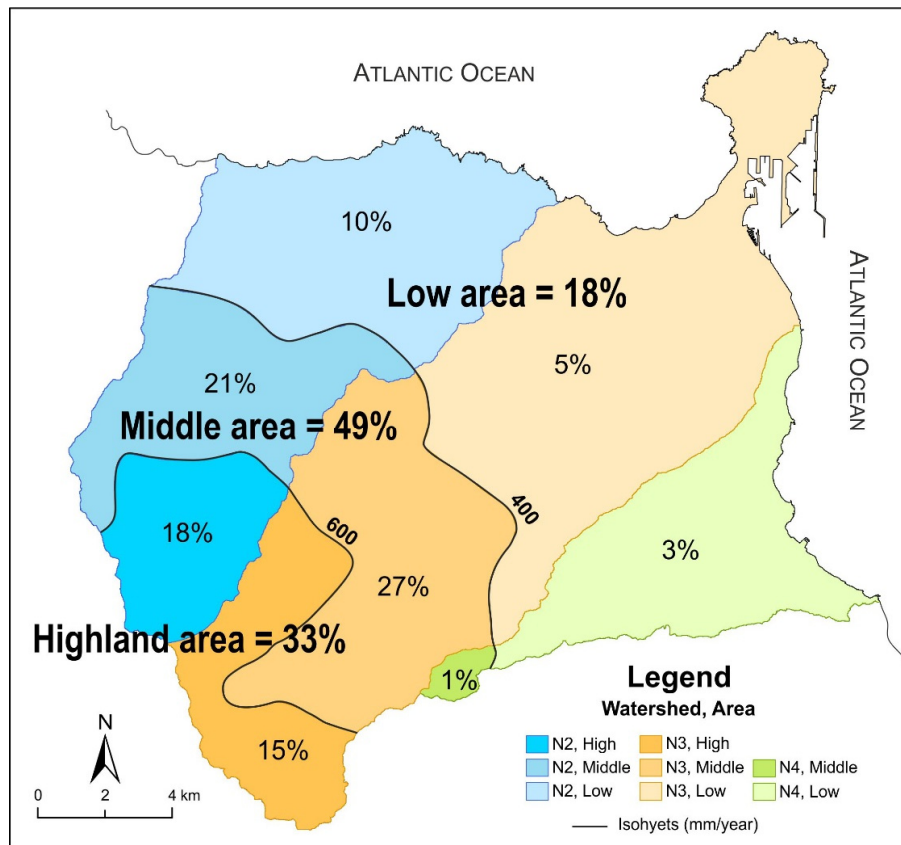

Figure 7. Fraction of the estimated average recharge in each subarea to total estimated recharge for all three studied watersheds (the whole study area) as a percentage. Small figures refer to each considered subarea and large ones to the respective hydrological zone (watershed).

The recharge estimation in the considered area, obtained by the chloride mass balance method, was about 28 hm^3/year, or 24% of the annual average precipitation. These results came close to, but were slightly higher than, the 19% precipitation recorded in the Island Water Plan [36], obtained by a non-specified water balance in soil. The application of water balance in soil to the same area [37] as part of the same project yielded a recharge of 15 ± 4 hm^3/year, which represents 13% ± 4% of precipitation, mainly in high and medium areas. This difference is not surprising because it was not possible to calibrate the daily water balance in soil with water table fluctuations or discharge measurements as these data are not available, and will probably never be obtained. This shows how the recharge estimation is uncertain and different methods may yield non-coincident or overlapping results [38].

This difference is also due to the fact that the two methods conceptually differ in terms of the averaging method and time scale. Thus the results may differ for the same conditions in the extensive area. In this case, the difference is due to neither the daily water balance method to estimate total

recharge nor to the CMB method to estimate net recharge (total recharge minus groundwater evapotranspiration by deep-rooted plants or direct evaporation from shallow water tables) as there is a thick non-saturated zone and no direct groundwater discharge to the land surface. The relative average rainfall during the considered period in relation to the long-term average was not taken into account. To increase the recharge estimation by daily water balance, the maximum soil water reserve used should lower and/or some preferential recharge through soil cracks and fissures must be allowed, and in accordance with field observations. The atmospheric chloride deposition balance estimates the long-term average net recharge when the groundwater chloride concentration from the top of the saturated zone is used, which was done. However, classical (Canarian) wells and the drainage crown of horizontal water-galleries and drills ("catas") somewhat penetrate into the saturated zone; springs mix groundwater and drilled wells penetrate deeply. The groundwater sampled and used as a proxy for recharge water does not represent locally recharged water, but is actually a mixture of local recharge with water from the up-flow. This results in dilution, which implies recharge overestimations. This overestimation is slight in high elevation areas, but may be somewhat relevant at medium altitudes, and quite significant in low areas.

Forestland may also trap atmospheric salinity by forest leaves' interception of dry particulate matter, which will be incorporated later on into local recharge through leaf fall, increasing chloride deposition with respect to what is collected as bulk deposition in open rainwater samplers. This may overestimate long-term recharge to some extent, and in an unknown quantity, mainly in lower parts of the study area. Direct studies of this effect have not been carried out.

6. Conclusions

The average total recharge volume in the considered area was estimated by contemplating that surface runoff was about 28 hm^3/year (92 mm/year), almost 24% of precipitation. This percentage would be 30% of precipitation should surface runoff not be taken into account. This result shows that accurate knowledge of runoff in the area would help improve recharge estimation by reducing the uncertainty of the calculated recharge, which cannot be well constrained with available data. The atmospheric chloride balance yielded higher recharge results than those derived from the water balance in soil. However, the latter values were non-calibrated, and may consequently be biased. The former may be overestimated to some extent, even after the major correction of taking runoff into account, and the latter may underestimate recharge as preferential recharge or lighter soils were not considered. This shows how recharge estimations are uncertain and how different methods may yield non-coincident or overlapping results, which are subject to their own uncertainties given the simplifications introduced and the use of biased proxies and parameters.

A first approach of the uncertainty is provided, which is quite high. It should be refined by extending the monitoring series and complementary data in the middle and high areas where recharge was mostly produced, especially in the eastern part. Studies should be extended to other areas of the island where recharge was potentially high. The fact that rainfall and recharge present quite a good relationship with distance to the coast helps correct the island surface slope effect on chloride concentration in the water samples from large springs and deeply penetrating wells. Yet such a linear

variation is not so clear for atmospheric chloride deposition, so new sampling stations would help improve trend variability estimations with radial orientation on the island.

According to the European Water Framework Directive and the Spanish Water Act, water plans have to be reviewed every 6 years. The Water Council of Gran Canaria is in charge of maintaining the monitoring network and should provide, operate and maintain the monitoring network needed to estimate recharge by the atmospheric chloride deposition balance method, which would reduce uncertainty. The same can be said of applying other methods and the data needed for calibration and validation. These other methods are necessary to make separate independent estimations of difficult-to-quantify recharge rates.

Author Contributions

Gema Naranjo performed the fieldwork, sample and data collections, and recharge calculations, and she prepared the manuscript with the help of the other authors; Tatiana Cruz-Fuentes performed sample collection and the curve-number method implementation. MCarmen Cabrera and Tatiana Cruz-Fuentes reviewed the manuscript. MCarmen Cabrera and Emilio Custodio conceived the original idea, and supervised the research, the manuscript and the results.

Conflicts of Interest

The authors declare no conflict of interest.

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