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Estimation of aquifer recharge by means of atmospheric chloride deposition balance in the soil

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Resum. En estat estacionari, la deposició de clorur atmosfèric sobre el terreny permet estimar la recàrrega mitjana en els aqüífers a llarg termini quan el contingut mitjà de clorurs de l'aigua de recàrrega és conegut. És un mètode senzill, ben conegut, però no sense dificultats teòriques i pràctiques, malgrat que el seu potencial, sovint, no s'aplica. En circumstàncies favorables els resultats obtinguts són fiables i permeten estimar-ne la incertesa. El contingut en clorurs de la recàrrega es pot deduir del mostreig de la part superior del nivell freàtic. El mètode i la seva millora han estat l'objectiu de recerca i d'aplicació en diversos aqüífers i en tot el territori espanyol, com a part de projectes de recerca aplicada i de tesis doctorals lligades al Grup d'Hidrologia Subterrània del Departament d'Enginyeria del Terreny, Cartogràfica i Geofísica, de la Universitat Politècnica de Catalunya (UPC). En el cas d'aqüífers que descarreguen en brolladors o són explotats mitjançant pous profunds, la mescla vertical de l'aigua recarregada a diverses altures és important, de manera que la recàrrega estimada a partir del balanç de clorurs pot ser notablement sobrevalorada i cal fer-hi correccions. El mètode es pot comparar favorablement amb els altres mètodes per a avaluar la recàrrega, encara que cadascun proporciona estimacions de la recàrrega diferents, que s'han de considerar en el context apropiat de lloc i temps.

Paraules clau: recàrrega · aqüífers · balanç de clorurs · Espanya · Catalunya · Illes Canàries

Abstract. The measurement of the atmospheric chloride deposition on land allows the estimation of long-term average aquifer recharge when the average chloride content in the recharge water is known. This is a well-established, simple method, although not exempt from theoretical and practical difficulties. In spite of its potential, it is seldom applied. Under favorable circumstances, the results are reliable and the associated uncertainty can be determined. The chloride content of recharge water can be obtained from sampling the top of the water table. The method and its improvements have been the subject of extensive research and it has been applied to several aquifers throughout Spain, in the context of applied research projects and in doctoral thesis studies, by the Groundwater Hydrology Group of the Geoengineering Department of the Technical University of Catalonia (UPC). For aquifers discharging into springs or developed by means of deep wells, the vertical mixing of groundwater recharged at different altitudes is important. Thus, the chloride content may overestimate aquifer recharge and corrections are needed. In the present study the method has been developed and improved. It compares favorably to other methods, although it yields diverse recharge estimations that have to be referred to the appropriated site and time.

Keywords: recharge · aquifers · chloride balance · Spain · Catalonia · Canary Islands

Introductory remarks

Aquifer recharge is the downward water inflow to the water table as a result of precipitation and, occasionally, surface water infiltration, including excess irrigation water. Under typical circumstances, precipitation is the main source of recharge, referred to as diffuse recharge, and it corresponds to the fraction of non-evapotranspirated water that flows downwards through the unsaturated (vadose) zone, from the soil root zone towards the water table. This implies a time delay as well as a smoothing out of the variability due to precipitation irregularity. Most rainfall infiltration is stored and flows through the pedologic soil, although a fraction may penetrate below the root zone depth through soil discontinuities, thus avoiding evaporation by solar radiation and plant capture. All this water adds to the downward flow through the unsaturated zone. Recharge through deep fractures receiving concentrated inflow from the surface or perched saturated water bodies may also avoid the root zone and be incorporated into the deep vadose zone and the water table. This is also a source of recharge to the aquifer that is integrated when groundwater is sampled at the water-table top. Together, these inputs represent the total recharge.

The water-table depth below the land surface determines the thickness of the unsaturated zone below the root zone and the possibility of direct phreatic water evaporation (transpira-

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tion) by plants or through soil heating by solar radiation. Surface water bodies, i.e., streams, lakes, and swamps, are a potential source of concentrated recharge when they are above the water table. This is a less common situation in relatively humid climates and not very permeable geological formations, but may be quite significant in permeable rocks as well as arid and semi-arid areas. It is also the case during snowmelt in nearby areas. This will not be further considered here since this paper refers mostly to diffuse recharge under Mediterranean climates, especially in regions with a conspicuous topographical relief and relatively deep water tables.

Knowledge about aquifer recharge is essential to evaluate aquifer renewable water resources for water studies and water management. But it is also one of the most difficult issues [19], due to the uncertainties arising from its inherent complexity, the large temporal and spatial variability, the paucity of observations, gaps in the data series, and a lack of defined parameters needed to apply recharge calculation codes. Reasonable results entail the application of as many different appropriate techniques as possible [41]. Unsaturated zone processes are essential [45] and should be carefully considered.

Aquifer recharge evaluation has been the subject of several books [16,33,43] and a large number of papers, mostly referring to local situations, but the subject is often insufficiently developed in hydrogeology textbooks, with only a few exceptions [13]. Well-equipped experimental areas to measure recharge are scarce, represent local situations, and correspond mostly to research stations. The practical problem is how to evaluate recharge–and, if possible, its uncertainty–for aquifer studies and management when information is largely incomplete.

Different methods can be used to evaluate recharge, yielding diverse results that refer to the timing (long-term averages, yearly values, per rain event) or to the areal extent (regional, basin-wide, or local). They rely on long-term knowledge of geological, soil, plant, and atmospheric dynamics, and on rainfall, stream-flow series, solar radiation, and climate observations. Since the data often include relatively few variables, calculation models should be simplified. In their current form, they often include empirical or semi-empirical terms with parameters derived from research areas that often are quite different from the real study area or basin. Only rarely the results from these models are accompanied by an estimation of uncertainty, nor are they subject to a sensitivity analysis. This is an important drawback since the uncertainty may be significant, as is the case in other hydrological estimations, including surface water outflow.

The most often used diffuse recharge evaluation methods rely on soil water balance, which may yield the event recharge values if input data are appropriate. Ideally, a daily time interval should be included as well. However, in the more recent studies and evaluations, the results are often aggregated to yield monthly, yearly, and average long-term values.

A model can be calibrated by comparing the results with the basin or aquifer outflow measured at gauging stations, or/and through water-table fluctuation analysis. However, hydrogeological circumstances may invalidate the results, such as when the aquifer surface area does not coincide with gauged watersheds, or the effective recharge area is unknown, or there is groundwater exchange with other aquifers, vertically and laterally.

In order to assess the evaluations derived from a given model, the use of other, independent methods is highly advisable, even if they are simple ones. The chloride balance method is the subject of this paper. While not novel [20,21], its application presents some difficulties that must be solved. The results are in the form of long-term recharge values, which is an aspect that must be taken into account in comparisons with data obtained by other methods.

The method of atmospheric chloride balance in the soil

Precipitation is a source of chloride, both dissolved in water and contained in dry fallout (dust). Under typical circumstances, almost all the dissolved chlorine is in the form of chloride ions. Since the main chloride source is the sea, it is often the most abundant salt dissolved in precipitation and contained in terrestrial dust, depending on geology, soil, and artificial deposits. The atmosphere contains several naturally volatile chloride compounds and human activities provide minor contributions. Chloride deposited on the land and vegetal surfaces is subsequently dissolved in water. It then infiltrates the soil, where the concentration increases due to evapotranspiration (actually, evapoconcentration, since chloride salts are nonvolatile), and becomes fully incorporated into the recharge.

Chloride is a conservative substance in most natural environments, which means that it remains in the water if its concentration is below of about 300 g/l. Even if there is some precipitation in dry seasons, chloride is mostly dissolved later on, except in very dry climates where it accumulates as salt crusts. In the long-term, it is not permanently exchanged with the solid medium although there may be some exchange with organic matter [7,39]. This means, at most, a small retardation effect that typically can be neglected. Thus, chloride behaves practically as an ideal tracer, present in concentrations that are easily measurable using the accurate common analytical approaches. The exception is when the chloride concentration in precipitation is low, in which case anion chromatography may be needed to obtain the desired accuracy.

In a given parcel of land, at a given time interval, the water and chloride balances in the root zone (values in water depth and mass, per unit surface) are:

$$P = R + ES - IES + \Delta S + CR + E \qquad (1)$$

$$P \cdot C_P = R \cdot C_P + ES \cdot C_{ES} - IES \cdot C_{ESI} + \Delta SC + CR \cdot C_{CR} + F \qquad (2)$$

where:

P	water precipitation on the land, as measured by a rainfall gauge, taking into account canopy processes
R	recharge leaving the soil root zone downwards
ES	outflowing surface runoff (overland and interflow) from the area

ESI	inflowing surface runoff from other areas that contribute to local infiltration
ΔS	change (increase) in root zone soil humidity
CR	concentrated recharge bypassing the soil root zone (through cracks, fissures)
E	evapotranspiration, which is chloride-free water vapor
C_P	average chloride concentration of P, including chloride dissolved from dry fallout, as measured in an integrated sample during a given time interval from an open precipitation sampler in which dust capture is similar to dry deposition on land
C_R	average chloride concentration in recharge water (see discussion later on)
C_{ES}	average chloride concentration in outflow runoff, measured in nearby creeks and including the atmospheric contribution and salts leached from the soil
C_{IES}	average chloride concentration in inflow runoff
ΔSC	change (increase) of soil root zone chloride storage
C_{CR}	average chloride concentration in water bypassing the soil root zone, which is assumed to be close to that of rainfall, with some weighting due to variability in the precipitation chemistry along a given rainfall event
F	other sources of chloride (chloride flow multiplied by the time interval), such as that from minerals or precipitated in the soil from previous dry periods, discounting what may be precipitated at the end of the period, if all this is not included in ΔSC

When the balance comprises a long time period under steady climatic conditions and stable plant cover, the soil and the unsaturated zone source terms cancel each other out or may be neglected, and runoff inflow is usually small or nil, except if there is local infiltration from snowmelt.

The long-term balances are:

$$\sum P_i = \sum R_i + \sum ES_i + \sum CR_i \tag{3}$$

$$\begin{aligned}\sum (P_i \cdot C_{Pi}) = \sum (R_i \cdot C_{Ri}) + \sum (ES_i \cdot C_{ESi}) + \\ + \sum (CR_i \cdot C_{CRi}) + \sum (F_i)\end{aligned} \tag{4}$$

where the short-term intervals or event durations are added to form the long-term balance.

$\sum (P_i \cdot C_{Pi}) \equiv \sum A_i$ is the total chloride deposition, A, being the deposition $A \equiv P \cdot C_{P_i}$

In developed soils in common rocks and sediments (excluding evaporites and recent unleached marine or saline lake sediments), F can be safely neglected. For practical applications, the following should be considered. A_i refers to the sampling protocol, which may be per precipitation event duration, daily, or monthly (or other time interval) when a composite sampling is obtained, always excluding evaporation and including dry deposition in periods without rain. ΣA_i should be derived from a complete series of years. However, discontinuities in the series are frequent such that interpolation is needed to fill in the gaps. Often, the observation period is not long enough, in which case the long-term value has to be estimated from records covering a period of one year or a few years. This increases the estimation uncertainty. A study carried out by Alcalá and the author, in which long data series obtained from Spanish stations were analyzed, indicated that long-term values are reasonably approached with 3–5 full years, ideally 10 years, although extraordinary rainfall events may be a disturbing factor.

The same can be said about $\Sigma(ES_i \cdot C_{ESi})$, which, fortunately, is often a minor term. It can be derived from gauging and sampling nearby creeks and brooks, when they carry mostly surface runoff. As such data are rarely available, ES_i is estimated (e.g., by using the curve-number method [24]) and the value of C_{ESi} is assumed to be close to that of the precipitation or slightly higher, to take into account possible leaching of temporarily deposited salts into the upper soil by evaporation of previously infiltrated water. This might be a small contribution in wet areas but significant in dry climates. Stream-flow chloride content may fluctuate due to the complex processes of runoff generation [42].

$\Sigma(C_{Ri} \cdot C_{CRi})$ should be assumed. C_{Ri} may be taken as a fraction of P_i, depending on soil characteristics and changes according to soil humidity. C_{CRi} may be safely assumed to be equal to C_{Pi}, or slightly higher, in case there is local runoff that concentrates the water over discontinuities.

R_i (or ΣR_i) is the unknown to be deduced from the balance equations; it is the diffuse recharge at the base of the soil root zone. When C_{Ri} is also at the soil root zone base, this value is not available, except in experimental areas. R_i is routed through the vadose zone down to the water table. This means a delay (days to months and even years depending on recharge rate and vadose zone thickness). Fluctuations are smoothed out due to dispersion and also to mixing with concentrated recharge. Recharge water is often obtained from the top of the local water table through very low penetration wells and boreholes. The chloride content of these samples represents local recharge only if transport through the vadose zone is steady. This means a short transport time relative to long-term changes in recharge and that the area is free from anthropic activity (changes in land use, such as deforestation, reforestation, forest management, and extensive agriculture), or that a new steady state has been attained after the changes were produced. This is not always the case in arid areas with deep water tables, as has been repeatedly documented in Australia. Sampling at the top of the water table includes concentrated recharge, avoiding the root zone; it thus represents total precipitation recharge, if there are no extensive preferential recharge areas.

If $\overline{C}_R$ is the average chloride concentration at the water-table top, then for a simple case:

$$R = \frac{\sum A_i - \sum (E_{Si} \cdot C_{ESi})}{\overline{C}_R} \tag{5}$$

or, for a series of n complete years, the average recharge value $\overline{R}$ is:

$$\overline{R} = \frac{\sum^{n} A_i - \sum^{n} (ES_i \cdot C_{ESi})}{n \cdot \overline{C}_R} \tag{6}$$

When surface runoff is negligible:

$$\overline{R} = \sum^{n} A_i / \left(n \cdot \overline{C}_R\right) \tag{6'}$$

The average value of $\Sigma\overline{A}_i \equiv \overline{A}$ can be related to the average $\overline{P}$ and $\overline{C_P}$

$$\overline{A} = \overline{P} \cdot \overline{C}_P + \overline{\varepsilon_{CP}} \cdot \overline{P} + \overline{\varepsilon_P} \cdot \overline{C_P} + \overline{\varepsilon_P \cdot \varepsilon_{CP}} \tag{7}$$

in which $\overline{\varepsilon_P}$ and $\overline{\varepsilon_{CP}}$ are the mean values of the deviation of P and C_P from the respective mean values. Only when P and C_P are normally distributed, are $\overline{\varepsilon_P}$ and $\overline{\varepsilon_{CP}}$ zero, $\overline{\varepsilon_P \cdot \varepsilon_{CP}}$, the mean value of the product $\varepsilon_P \cdot \varepsilon_{CP}$, is a small value for uncorrelated variables, but this is not the case for correlated variables when they are spread (the statistical treatment is outside the scope of this paper). Thus, $\overline{A}$ does not coincide with $\overline{P} \cdot \overline{C}_P$. The greater the distribution spread (larger standard deviation), the greater the difference. When statistical distributions are not normal, the difference also increases. These facts are often neglected when data are scarce and the product of means is the only way to estimate the values, but this adds to the uncertainty.

The same can be said for chloride outflow with surface runoff, $\overline{O} = \frac{1}{n}\sum^{n} ES_i \cdot C_{ESi}$, which is often obtained from the product $\overline{ES} \cdot \overline{C_{ES}}$, with similar considerations as noted above.

A rather simple example, reproduced from the results of a 2-year, north-south rainfall sampling on Gran Canaria, is presented in Table 1 [25,26]. Monthly samples from open samplers were collected, protecting them from evaporation by a liquid paraffin layer. The results shown here are from the north-facing side of the island, which receives orographically enhanced rainfall.

The uncertainty of $\overline{R}$, measured by the standard deviation, σ_R, or the coefficient of variation, $CV_R = \sigma_R/\overline{R}$, for normally or close to normally distributed variables, is easily obtained [8]:

$$\sigma_R^2 = \sum^{n}\left[\left(\frac{\partial f}{\partial x_i}\right)^2 \cdot \sigma_{x_i}^2\right] \tag{8}$$

where x_i is one of the n variables in the calculation of R from a function f, and the σ_{xi} are the respective standard deviations.

$$\text{For } \overline{R} = \left(\overline{A} + \overline{O}\right) / \overline{C_R}; \quad \sigma_R^2 = \frac{\sigma_A^2 + \sigma_O^2 + \overline{R}^2 \sigma_{CR}^2}{\overline{C}_R^2} \tag{9}$$

$$\text{For } \overline{R} = \left(\overline{P} \cdot \overline{C_P} + \overline{ES} \cdot \overline{C_{ES}}\right) / \overline{C}_R;$$

$$\sigma_R^2 = \frac{\overline{C}_P^2\, \sigma_P^2 + \overline{P}^2\, \sigma_{CP}^2 + \overline{C}_{ES}^2\, \sigma_{ES}^2 + \overline{ES}^2\, \sigma_{C_{ES}}^2 + \overline{R}^2\, \sigma_{CR}^2}{\overline{C}_R^2} \tag{10}$$

Meaning of the $\overline{R}$ value

For a given site with known soil humidity, vegetation cover, and slope characteristics, the value of ES can be deduced, or measured when possible, which allows determination of the value of $\overline{R}$. For a permeable soil in flat land, ES is small provided that the ground does not become water-logged or frozen, in which case recharge is temporarily or permanently rejected. A non-negligible or negative value of $\overline{R}$ suggests errors in the estimation of $\overline{A}$, $\overline{ES}$, $\overline{C}_{ES}$, or non-representative $\overline{C}_R$ values.

In areas of poorly permeable soil, the ES value is large and the top of the water table may be influenced by groundwater from other areas, in which case the estimated $\overline{R}$ value is not representative. The same can be said if there is a permafrost layer or if the area is often flooded. When the water-table surface is at or near the land surface, soil water samples may correspond either to a groundwater outflow that was recharged in other upflow areas or to near-surface evaporated water.

Therefore, the regionalized, estimated $\overline{R}$ value and its uncertainty are virtual values that are only real when the conditions for a water-table aquifer below a sufficiently thick vadose zone are met. In a relatively large water-table aquifer with scarce surface water outflows, $\overline{R}$ represents the recharge to a large water-storage area, which means a long residence time. However, for rough terrain, e.g., in poorly permeable rocks, recharge corresponds to small water-storage aquifers and thus to a short residence time, with conspicuous seasonal and interan-

Table 1. Chloride deposition in five stations along a northern–centre, coast to highland transect in Gran Canaria island, showing the difference between calculation from montly deposition and from the mean values product. The $\overline{P} \cdot \overline{Cl} \equiv A^*$ value is systematically higher than $\overline{A}$ value, thus overestimating chloride deposition. Chloride deposition decreases with elevation, except for station 217, which is affected by westerly winds, while the others reflect NE trade winds. Some voids in the concentration series were completed by interpolation or by correcting the ratio of days with samples from the total days of the period (source of raw data [25])

Station	Elevation M	no. days	ΣP_i mm	ΣA_i g m^{-2}	$\overline{A}$ g m^{-2} a^{-1}	$\overline{P}$ mm/a	$\overline{C}$ mg/L	$\overline{P} \cdot \overline{C}_P \equiv A^*$ g $m^{-2}a^{-1}$
73	475	710	1095	22,7	11.7	563	27.5	15.5
22	485	682	920	19,6	10.5	492	31.1	15.3
255	1020	672	1342	19,7	10.7	729	18.3	13.3
43	1520	713	977	15,8	8.1	500	17.3	8.7
217	1680	589	1251	28,5	17.7	775	28.7	22.3

Σ is the summation over the sampling period.
P_i is the monthly rainfall in a given time interval.
A_i is the monthly product of rainfall and sample chloride concentration in the same time interval.
$\overline{P}$ and $\overline{A}$ are the mean values over two years.
$\overline{C}_P$ is the mean chloride content of the rainfall sample series.

nual fluctuations and often with near-by drainage into creeks and brooks.

The evaporation of shallow water tables by plants or solar radiation increases C_R; thus, the estimated recharge becomes an effective recharge to the aquifer, which is less than the amount deduced from soil water balance calculations [44] or from sampling of vadose zone water, as commented on below. Therefore, the chloride water balance yields recharge values whose interpretation depends on local hydrogeological conditions. The more extreme the conditions and the more arid the climate, the greater the uncertainty.

Recharge water average chloride content

When the unsaturated zone is sampled by means of soil extraction using hand excavation (for shallow depths), manual augers (for depths up to a few meters), or core drilling, the soil water chloride content can be determined by laboratory testing (dilution with water, squeezing, displacement by an immiscible fluid, etc.) and a vertical chloride content profile drawn. This procedure is often repeated at different sites to acknowledge spatial variations.

These profiles represent the recharge penetration during a fraction of a year for shallow water tables, or over a period of years for not-so-shallow water tables, or several years, even centuries, for relatively deep water tables [34,40]. Sometimes, chloride content fluctuations depend on the mass balance of each recharge event, when the water moves downwards and changes are smoothed out by diffusion-dispersion processes. This phenomenon increases with increasing depth and the time elapsed from the corresponding recharge event.

The average value–or the deeper unsaturated zone value if sufficiently smoothed out–must coincide with the chloride concentration in the upper water table. This is the most frequent case. However, differences occur under the following conditions: (i) there is a deeply penetrating concentrated recharge; (ii) there is diffusion from a water-table aquifer in which recharged upflow predominates; (iii) actual recharge is affected by anthropic changes (deforestation, cultivation, etc.) and moves downwards through the vadose zone; or (iv) the top of the sampled water table is affected by the diffusion effect of allochthonous groundwater below, as in coastal areas with a shallow marine wedge or thick mixing zone.

In thick unsaturated zones in dry climates, i.e., minimal recharge, the effect of past climate changes may still be moving downwards in the ground, such that water entering the water table is not current recharge but rather recharge from previous conditions.

Effect of the upslope recharge contribution on groundwater samples

Pumped groundwater samples are commonly mixtures of water recharged at different times and locations, except for point boreholes. In the latter, the sample does not necessarily represent the local water-table top, but water traveling along a flow line and recharged elsewhere. Water mixing is a common circumstance for springs, long-screened wells, and base-flow streams. Therefore, samples do not yield a C_R value as defined previously. The chloride content of these samples, C_M, corresponds to a weighted mixture of water from different flow lines. In practice, assuming the water sample was obtained such that it is representative of the aquifer (no evaporation, no water stored in the well tube, no mixing with surface water, no remnants of drilling fluids, etc.), the C_M value can be used to determine the total aquifer recharge rates over the aquifer catchment area, if a realistic mixing model is adopted. Several possibilities are discussed below. These apply to sloping aquifers either with parallel flow lines, such as in the slopes of valleys or linear coastal areas, or with divergent flow lines, such as in the slopes of small round islands, mainly high volcanic islands above and down-flow from the volcanic "core" [11].

Let us consider the simplified situation depicted in Fig. 1, in which H is the land elevation, and h the water-table elevation, both above the discharge line (a major river, the coast, a large lake, a very pervious aquifer). Let P be the average precipitation, and R the average recharge, with respective average chloride contents of C_P and C_R that vary with location. A steady state is assumed and the negligible effect of runoff is disregarded or its effect was previously discounted from the rainfall contribution.

Given parallel flow lines, with water and mass (chloride) balances per unit width at distance l from the divide and x being an intermediate-distance dummy integration variable, then the flow per unit width at l is:

$$\text{Water balance } q_l = \int_o^l R(x)\,dx \tag{11}$$

$$\text{Mass balance } q_l^c = \int_o^l R(x)\,C_R(x)\,dx \tag{12}$$

$$C_M = \frac{q_l^c}{q_l} = \frac{\int_o^l R(x)\,C_R(x)\,dx}{\int_o^l R(x)\,dx} \tag{13}$$

where C_M represents the average chloride concentration along distance l.

Chloride concentration in the top of the water table at distance l is $C_R(l)=A(l)/R(l)$, which may be very different from C_M at the same site (Fig. 2).

For divergent flow lines (flow in a wedge-shaped aquifer), the same reasoning can be applied, in which case r is the distance to the apex, and ρ the dummy integration radius. Flows are total flows through the section.

Water balance per unit angle (radians)

$$Q_r = \int_o^r r\,R(\rho)\,d\rho \tag{14}$$

Mass balance per unit angle (radians)

$$Q_r^c = \int_o^r \rho\,R(\rho)\,C_R(\rho)\,d\rho \tag{15}$$

$$C_M = \frac{Q_r^c}{Q_r} = \frac{\int_o^r \rho\,R(\rho)\,C_R(\rho)\,d\rho}{\int_o^r \rho\,R(\rho)\,d\rho} \tag{16}$$

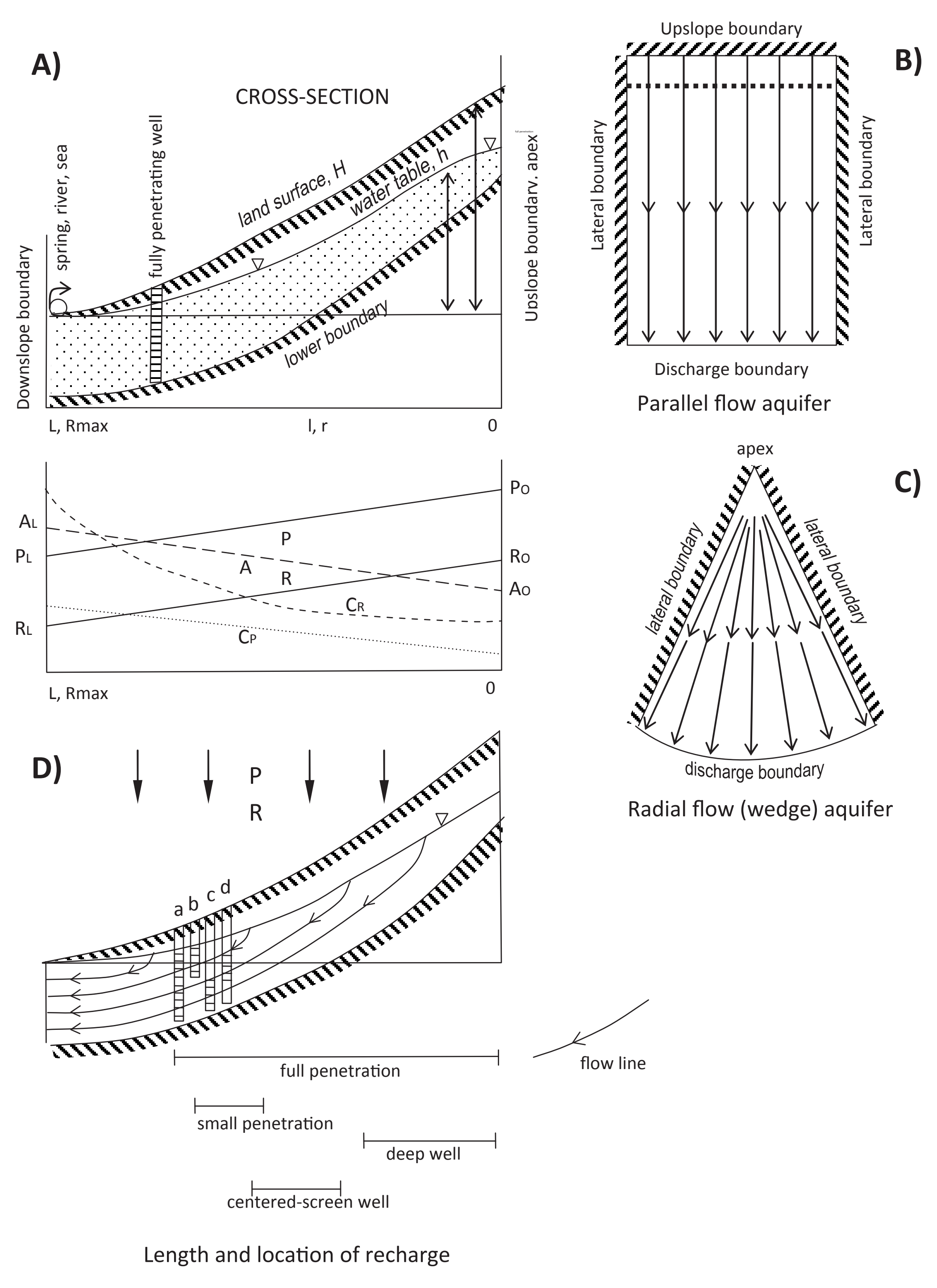

Fig. 1. Recharge in a slopping aquifer. (**A**) Cross-section and P (precipitation), R (recharge), A (atmospheric chloride deposition), C_P (chloride concentration in rainfall), and C_R (chloride concentration in recharge): qualitative variation along the flow. (**B**) Parallel flow aquifer. (**C**) Radial-flow aquifer. (**D**) Length and location of areal recharge mixing in wells according to the screen length and position, assuming the well does not significantly disturb of the groundwater flow pattern.

As in the former case, the chloride concentration at the top of the water table at distance r is $C_R(r) = A(r)/R(r)$ (Fig. 2).

C_R can vary greatly and non-linearly from the top down, so that it is more conveniently referred to the smoother variable A, being $A \equiv R(l) \cdot C_R(l)$ or $A \equiv R(r) \cdot C_R(r)$. In this case equations (13) and (16) become:

$$C_M = \frac{\int_o^l A(x)\,dx}{\int_o^l R(x)\,dx} \quad \text{for parallel flow} \qquad (13')$$

$$C_M = \frac{\int_o^r \rho\, A(\rho)\,d\rho}{\int_o^r \rho\, R(\rho)\,d\rho} \quad \text{for radial flow} \qquad (14')$$

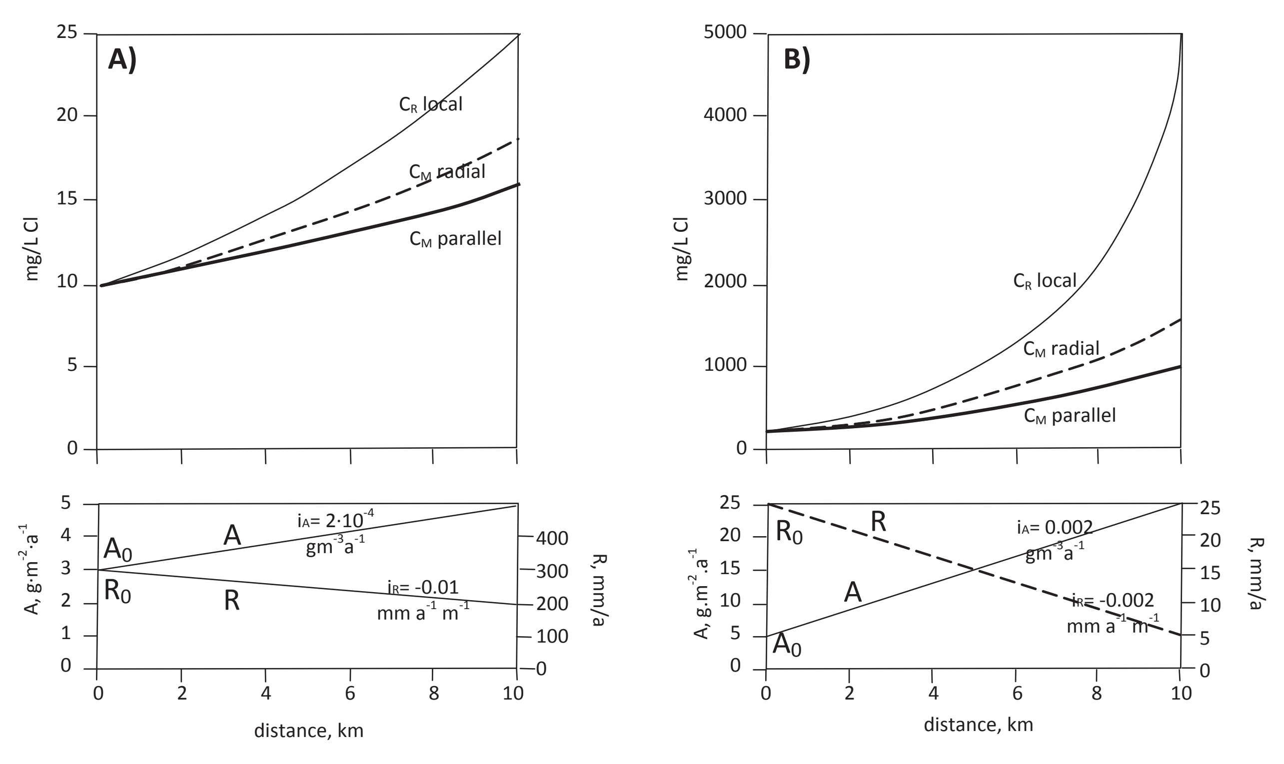

Fig. 2. Recharge in a sloping aquifer, showing chloride concentration in local recharge and the average value through the aquifer thickness, at increasing distance from the upslope boundary or apex in parallel flow and radial flow, respectively. (**A**) Well-recharged aquifer (humid climate) with slightly changing, moderate chloride deposition. (**B**) Poorly recharged aquifer (arid climate) with changing chloride deposition (proximity to the coast).

Let us consider linear variations of R and A, with R generally decreasing and A generally increasing when l or r increases.

Considering the slopes of R and A, from the top down (negative if decreasing), designated as i_R and i_A, respectively, the linear variations are:

$$R(x) = R_O + i_R x \quad ; \quad R(\rho) = R_O + i_R \rho \tag{17}$$

$$A(x) = A_O + i_A x \quad ; \quad A(\rho) = A_O + i_A \rho \tag{18}$$

where R_o and A_o are, respectively, the recharge rate and the atmospheric chloride deposition at the upper boundary or apex.

$$C_M = \frac{2A_O + i_A l}{2R_O + i_R l} \equiv \frac{2 + (i_A/A_O)l}{2R_O/A_O + (i_A/A_O)l} \text{ (parallel flow)} \tag{19}$$

$$C_M = \frac{3A_O + 2i_A r}{3R_O + 2i_R r} \equiv \frac{3 + 2(i_A/A_O)r}{3R_O/A_O + 2(i_A/A_O)r} \text{ (radial flow)} \tag{20}$$

For known average chloride concentrations from deeply penetrating wells and main springs, profiles of C_M vs. l or r can be drawn. The unknowns are R_O/A_O, i_R/A_O, and i_A/A_O, which ideally can be obtained by mathematical optimization methods, if the profiles are well defined; that is, when $A_O \equiv A$ and $P_O \equiv P$ do not change over the aquifer catchment area, $C_M = C_O \equiv C$, as expected.

If i_A is small enough, $A_O \equiv A$ is the appropriate aquifer catchment value:

$$\begin{aligned} &\frac{1}{C_M} = \frac{R_O}{A} + \frac{i_R}{2A} l \quad \text{(parallel flow)} \\ \text{and} \quad &\frac{1}{C_M} = \frac{R_O}{A} + \frac{2}{3}\frac{i_R}{A} r \quad \text{(radial flow)} \end{aligned} \tag{21}$$

which are straight lines in the plot of $1/C_M$ vs. l or r, with the intersect R_O/A and slope $\frac{i_R}{2A}$ and $\frac{2}{3}\frac{i_R}{A}$, respectively.

Usually, $|i_A| \leq |i_R|$, so it is convenient to write equations (19) and (20) as:

$$\begin{aligned} &\frac{1}{C_M} = \frac{2R_O/A_O + (i_R/A_O)l}{2 + (i_A/A_O)l} \text{ (parallel flow)}; \\ &\frac{1}{C_M} = \frac{3R_O/A_O + 2(i_R/A_O)r}{3 + 2(i_A/A_O)r} \text{ (radial flow)} \end{aligned} \tag{22}$$

A plot of $1/C_M$ vs. l or r results in a curved line (approximately a straight line when i_A is small) from which the coordinates of three points distributed along it can be drawn in order to solve for the unknowns.

Simple application examples

The Anoia aquifer system. The Anoia aquifer system (about 50 km west of Barcelona), also known as the Carme-Capellades-Sant Quintí de Mediona aquifer, is a carbonated rock sequence dating from the Triassic to Eocene Age. It folds and dips to the north and is bounded by thrust faults and more re-

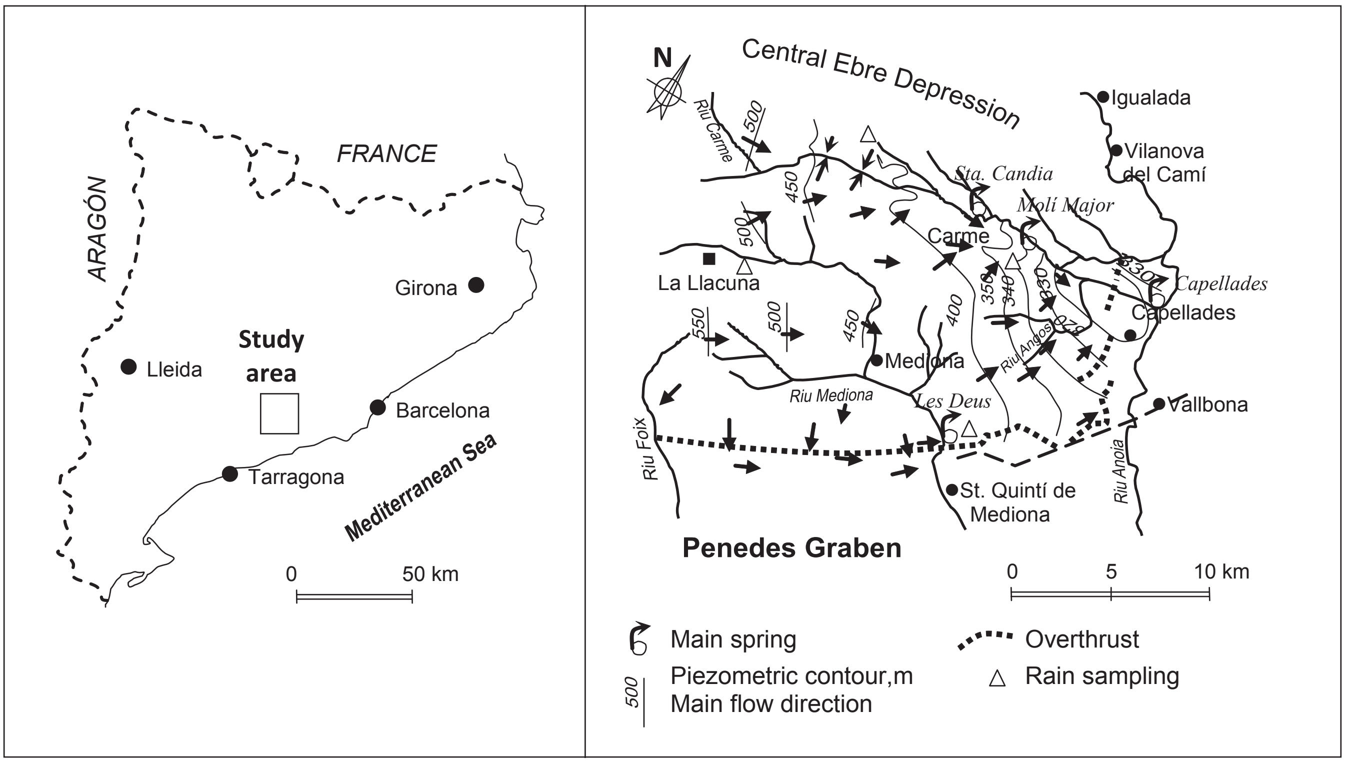

Fig. 3. The Anoia carbonate aquifer system (pre-littoral Catalan range, Barcelona) and the main discharge points (springs and the base flow of the Riera de Carme). The arrows indicate groundwater flow in the main recharge area [14,32].

cent clayish sediments. The Anoia system comprises three main overlapping aquifers, with intercalated gypsiferous layers [13,14,32]. Altitude differences in the catchment are about 300 m. Discharge from the aquifer system is through several large springs at the Anoia's boundaries and a permanent stream (Riera de Carme) (Fig. 3), around which most wells concentrate. Therefore, water samples are mostly compound (mixed) ones. Only a few small springs and boreholes allow samples to be obtained from the recharge area.

The average precipitation is about 600–650 mm/ year. Five open precipitation samplers were installed for monthly integrated sampling for about 2 years; only small differences among the samples were noted. The average chloride concentration was around 5.5 ± 1.0 mg/l. Table 2 shows the recharge estimate, in which surface runoff chloride exportation was considered to be negligible. The aquifer slope effect was not important due to the rather homogeneous areal atmospheric deposition of chloride.

The total average recharge rates correspond to the average values for the areas feeding either the springs or the Riera de Carme aquifer [32]. To obtain an independent estimate of recharge, tritium was sampled during two periods separated by more than a decade. This allowed the decreasing trend to be quite well defined and mixing models to be applied [16], and, in turn, the average groundwater turnover times in the main springs to be determined. The well-mixed (exponential) model, with piston-flow components for confined areas, resulted in turnover times that increased from 10–15 years at Santa Candia (Table 2) to up to 40–60 years at Les Deus. Considering aquifer water volumes, these results indicated average recharge values of the same magnitude as those shown in Table 2. Tritium sampling of small springs and of a well inside the area for a period of 2 years indicated probable local turnover times of 10–15 years [32], consistent with the estimated average recharge rates.

Table 2. Estimation of recharge in the Anoia aquifer system after regionalizing data [32]. Surface runoff is small and has been neglected. Values are given as X±σ, being X the magnitude and σ its standard deviation. See Fig. 3 for the sites. Results are too uncertain for Molí Major and Capellades

Site spring	$\overline{P}$ mm/a	$\overline{A}$ g m^{-2}a^{-1}	$\overline{C}_R$ mg/L Cl	$\overline{R}$ mm/a	$\overline{R}$ / $\overline{P}$	Situation
Santa Candia	625±25	3.3±1.1	16±5	205±70	0.33±0.11	Carme stream
Molí Major	640±40	3.5±1.9	18±6	195±124	0.30±0.19	Carme stream
Cal Tort (stream)	675±25	3.3±1.1	25±6	130±55	0.19±0.08	Carme stream
Capellades	650±35	3.5±1.1	21±5	165±65	0.25±0.10	E boundary
Les Deus	600±25	2.9±2.5	23±4	125±110	0.21±0.31	Mediona stream

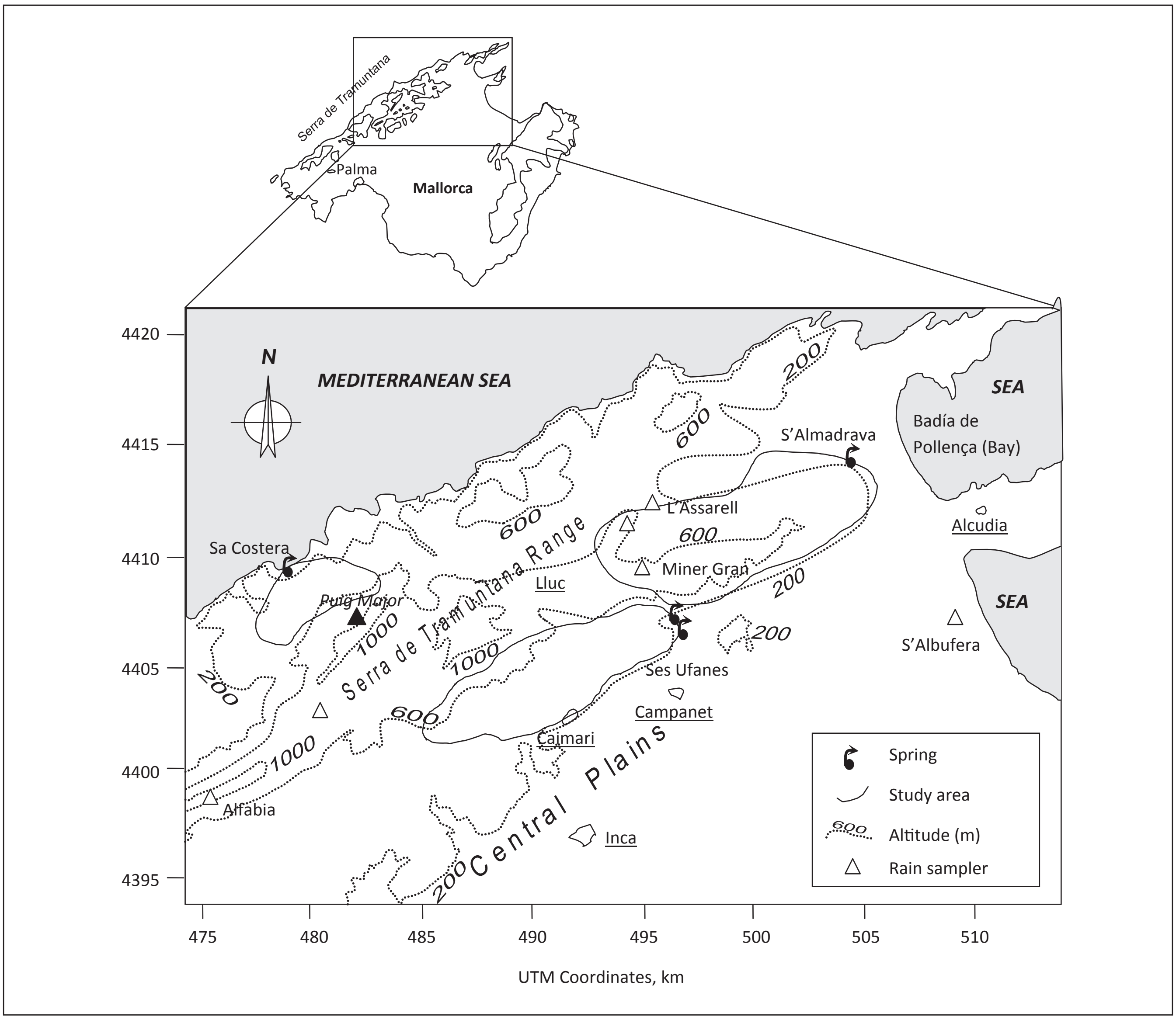

Fig. 4. The eastern Serra de Tramuntana range in the northern part of Mallorca. The bounded recharge areas correspond to the three main outflow springs: Sa Costera, the intermittently large spring Ses Ufanes, and S'Almadrava. Ses Ufanes is an overflow spring of the upper catchment area, with the remaining flow contributing to the S'Almadrava area.

Areal recharge in the eastern Serra de Tramuntana range, Mallorca Island. The abrupt Triassic, Jurassic, and Cretaceous carbonated formation of the Serra de Tramuntana, in the northwestern part of the island of Mallorca, is a potentially important source of fresh groundwater that complements the supply of Palma de Mallorca (the capital) and the towns along the island's northeastern corridor. The complex geological structure of the formation [9] includes important aquifers that discharge either through springs or to the sea through the more recent (mostly Miocene) coastal sediments along the eastern side. The outflows are only known approximately. Rainfall in the highlands exceeds 1000 mm/year (up to 1350 mm/year) and decreases towards the coast, where it amounts to over 700 mm/year.

Three sectors in the eastern part of the range were selected for study (Fig. 4), corresponding to three main springs that drain extensive areas, as in common in karstic aquifers. Open collectors were used to sample atmospheric water on a monthly basis for about 2 years at four sites. The results are shown in Table 3.

The C_P values in Table 4 are clearly overstated due to the large dispersion and non-normality of the statistical distribution. Therefore, they are poorly reliable for estimating recharge.

Table 3. Average atmospheric chloride deposition rates in eastern Serra de Tramuntana range [9]. Excluding Miner Gran, in the downwind side, A is relatively homogeneous

Site	Altitude, m	A, g $m^{-2}a^{-1}$Cl	Comments
Alfabia	1000	13.4	Highlands
Miner Gran	600	20.2	Downwind; east
S'Assarell	400	12.7	East
S'Albufera	1	12.8	East wetlands; littoral

Table 4. Estimation of average recharge rates in the catchment areas of the three study main springs of eastern Serra de Tramuntana range. $A^* = \bar{P} \cdot \bar{C}_P$; $\bar{P}$, σ_P, $\bar{R}$, σ_R mm/a; $\bar{A}$, $\bar{A}^*$, σ_A, g $m^{-2}a^{-1}$; C_R, σ_{CR} mg/L Cl; $\bar{R}$ / $\bar{P}$ dimensionless

Area	$\bar{P}$	$\bar{A}$	C_P	$\bar{A}^*$	C_R	$\bar{R}$	$\bar{R}/\bar{P}$	Comments
Sa Costera	900	13	15	13	30	435	0.48	Almost barren karst
Ses Ufanes	800	13	13	10	45	290	0.36	Sparse forest on carbonates; intermittent spring
S'Almadrava	750	13	17	13	60	215	0.29	Patchy forest on carbonates

Estimated uncertainty measured by σ (standard deviation).

Area	σ_P	σ_A	σ_{CR}	σ_R	$\sigma_{R/P}$
Sa Costera	100	1.0	5	80	0.10
Ses Ufanes	100	1.5	10	70	0.10
S'Almadrava	100	1.5	5	30	0.06

Recharge values correspond to the spring catchment area and agree with the estimated spring outflow and calculations based on soil water balances. The land surface is almost bare at Sa Costera basin but is sparsely forested in the Ses Ufanes basin and patchy forested in the S'Almadrava basin. Evapotranspiration increases and precipitation decreases from the Sa Costera basin towards the S'Almadrava spring; hence, recharge diminishes accordingly. In these three cases, chloride export from the spring catchment areas by surface runoff is small or negligible. Atmospheric chloride deposition seems rather homogeneous over the territory. Important sloping aquifer effects were not expected and thus explains why $\bar{R}$ / $\bar{P}$ values have not corrected by altitude changes.

Recharge in the El Abalario area, Doñana, Huelva. The large territory now known as Doñana, one of the main natural reserves of Europe, is in the southwestern part of the Iberian Peninsula, in the provinces of Huelva and Seville. The area contains a large aquifer in Quaternary fluviomarine sands with a blanket of recent eolian sands, an important feature favorable to recharge. An accurate determination of recharge is crucial to obtaining a good compromise between the preservation of natural resources and the supply of human needs, mostly for irrigation.

The main recharge area is El Abalario, located in the western sector. Recharged groundwater flows radially to the coast, to the contact with the large marsh, and to several permanent small streams, mainly to La Rocina creek, with areas of water-table evaporation in temporal lagoons and phreatophyte patches. Overall, El Abalario has a smooth, rolling sandy surface with a gently varying sub-humid Atlantic climate. Winds come mainly from the southwest, over the ocean.

Attempts to estimate recharge using diverse methods have been carried out and are currently under way [46–49], including determination of atmospheric chloride balance in the soil [7,30,31,35]. Accordingly, atmospheric chloride deposition samplers were established in five sites for a period of more than 2 years. The results, summarized in Table 5, allow estimation of the recharge values shown in Table 6.

At some sites, the unsaturated zone was periodically sampled for chloride and water content over a period of 2–3 years, preferentially after rain events. Based on atmospheric chloride deposition, an estimation of recharge, R, was obtained from each profile by calculating chloride accumulation [18,30]. The water-table depth in the sampled points was 1.0–1.5 m. The results are shown in Table 7.

For the same sites, values from Table 7 were higher than those of Table 6 since recharge calculations in the former correspond to recent recharge, ≤1 year. While the sampled period (1994–1996) was a humid one, $\bar{R}$ represents a longer period, a few years, partially corresponding to an average rainfall period. This explains why the average chloride content of water in the profile was somewhat less (more dilute) than the sampled top water-table water. Values calculated by other methods were similar, except for the artificial tracing recharge in bare dune soil (in a firebreak), which is a poorly representative situation.

The shallow water table in a portion of the area allows groundwater evapotranspiration, especially at sites that were previously forested with eucalyptus trees, now eradicated. This is reflected in the soil water balance, as recharge values deter-

Table 5. Estimation of $\bar{A}$ in Doñana and close–by areas. P mm/a; C_P mg/L Cl, $\bar{A}$ g $m^{-2}a^{-1}$

Station	$\bar{P}$	C_P	$\bar{A}$	Comments
Coast	600	7	6	At the shore
El Acebuche	550	8	3.5	Close to the coastal area
Los Cabezudos	600	4	4	Northern boundary, to the west
El Rocío	550	7	6	Northern boundary, to the east
Almonte	600	7	6	To the north, outside the main area
Sevilla	600	10	11	100 km to the NE, coastal and urban influence

Table 6. Average estimated recharge rates in El Abalario area (Doñana). Magnitudes are given by X±σ, the mean value and the standard deviation. Results are rather to quite uncertain

Area	$\overline{P}$ mm/a	$\overline{A}$ $g\ m^{-2}a^{-1}$	$\overline{C}_R$ mg/L	$\overline{R}$ mm/a	$\overline{R}/\overline{P}$
Coastal strip	550±50	6±3	64±15	95±50	0.17±0.09
Back dune strip	600±50	4±2	28±4	145±75	0.24±0.13
El Abalario dome	600±50	3.5±2	25±4	140±85	0.23±0.14
La Mediana old lagoons	650±50	3.5±2	21±4	165±100	0.25±0.16
South of La Rocina creek	600±50	3.5±2	28±7	125±80	0.21±0.15
North of La Rocina creek	650±50	3.5±2	50±7	70±40	0.11±0.06
La Vera ecotone	600±50	4.5±2	36±11	125±70	0.21±0.12

mined by a soil water balance approach are higher than those derived from mathematical models [46,49], as the former does not consider water-table uptaking by phreatophytes.

Recharge estimation in the Canary Islands. Data on atmospheric chloride deposition in the Canary Islands are scarce, although there is a N-S transect on Gran Canaria [25,26], partly described in Table 1, and additional data on the western La Aldea (Gran Canaria) watershed [37]. Information is also available for central Fuerteventura [27] and takes into account its arid condition, oceanic influence, windy environment, and small land barriers.

In Gran Canaria Island, the chloride content distribution in groundwater is mostly from wells that partially penetrate the aquifer and represents a mixture of locally recharged water with water recharged upslope. The mixing effect increases downslope, but there are also areas in which downward flow is hindered by the partly buried old caldera rim of the island, assumed to be of very low permeability. The thickness of the unsaturated zone is generally tens up to several hundred meters, except near the coast. This effect resembles the one illustrated in Fig. 1. In the area of the Guiniguada-Tenoya watersheds, in the north-east [38], a roughly continuously sloping aquifer, recharge varies from about 650 mm/year at the top to almost nil at the coast.

In the arid southeastern part of Gran Canaria, known as the Amurga phonolitic massif, close to ideal conditions are met, since the aquifer is wedge-shaped, positioned between two deep creeks (barrancos) that are open to the sea [10,17,25,26]. The average recharge rate at the apex is 30 mm/year and nil at the coast. According to environmental radioisotope data from deep wells penetrating the thick unsaturated zone, tritium levels are below measurement accuracy (±0.1 tritium units). This excludes the possibility of significant recent recharge reaching the water table, either diffuse or concentrated, or through the bore walls. The low radiocarbon content indicates a ^{13}C-corrected, piston-flow average residence time of about 11,000 years, with a small spatial variation since the wells are close to the coast. This apparent age can be explained by adding the downward flow time through the unsaturated zone and the time for the recharge to flow horizontally through the aquifer to the sampled well. The addition of them is integrated upslope from the wells. This process as well as the mixing can be easily formulated by considering ^{14}C as a non-sorbed tracer that decays in the ground, similarly to the case for chloride. The resulting equation does not have a closed-form solution, but an approximate solution yields an average recharge of 3–5 mm/year and up to 20 mm/year near the top, where the surface area is small. These long travel times imply that the sampled water was recharged under past climatic conditions.

A critical point in this approach is attributing an age to the radiocarbon content, since there is the possibility of incorporating dead (non-radioactive) carbon from minerals filling the fissures or by diffusion of deep volcanic CO_2. In fact, the high bicarbonate content of groundwater favors the latter process, although a thick unsaturated zone may also favor open-system rock weathering by downward diffusing CO_2 generated in the thin, poorly vegetated soil and from the atmosphere.

In the central part of Fuerteventura (old Betancuria massif and surroundings), the climate is arid and atmospheric chloride deposition is high due to the proximity of the sea, the windy environment, and the moderate altitude [27–29]. Since the climate is arid, only 31 precipitation samples were obtained from four sampling stations operated for more than 2 years. The results are given in Table 8. The coherence of these data is poor due to the paucity of samples and the irregular precipitation, which hinders good characterization of the series. In any case, recharge is low, about 1 mm/year in the valley but reaching

Table 7. Recharge rates deduced from soil water chloride content profiling in the Doñana area

Site	Forest characteristics	R mm/a	R/P
El Abalario road	Pine trees on dunes	210–260	0.31–0.32
El Acebuche	Deforested dune	255	0.33
El Asperillo	Pine trees, back–dunes	200–260	0.29–0.32
Casa del Gato (Cabezudos)	Eucalyptus trees, sands	265–290	0.37–0.40

Table 8. Recharge rate estimation for arid Central Fuerteventura island. Values are more uncertain than the ones shown due to the scarce samples, precipitation irregularity and non–normality distribution. $A^* = \overline{P} \bullet \overline{C}_P$; $\overline{P}$, σ_P, $\overline{R}$, σ_R mm/a; $\overline{A}$, $\overline{A}^*$, σ_A g m^{-2}a^{-1}; C_R, σ_{CR} mg/L Cl; $\overline{R} / \overline{P}$ dimensionless. Results are too uncertain

Area	Area characteristics
Pozo Negro	Central E coastal area, “malpais”
Pájara	Central area, old volcanics
Tuineje	Central area, some runoff, old volcanics
Morro de Velosa	Betancuria highland old volcanic complex

Area	Altitude m	$\overline{P}$	$\overline{A}$	$\overline{C}_P$	$\overline{A}^*$	$\overline{C}_R$	$\overline{R}$	$\overline{R} / \overline{P}$
Pozo Negro	90	80	6	10–80	1–6	2800	2.1	0.026
Pájara	190	115	8	30–70	3–8	9200	0.9	0.008
Tuineje	200	115	10	20–50	2–6	3500	2.9	0.025
Morro de Velosa	680	195	5	10–30	2–6	1350	0.4	0.002

Estimated uncertainty measured by σ (standard deviation).

Area	σ_P	σ_A	σ_{CR}	σ_R	$\sigma_{R/P}$
Pozo Negro	25	2	600	0.85	0.013
Pájara	30	5	200	0.55	0.005
Tuineje	30	8	600	2.3	0.007
Morro de Velosa	70	4	250	0.1	0.001

5 mm/year in the Betancuria massif highlands, albeit with large uncertainty. The area is sparsely vegetated, with thin soil.

As a last example, on Gomera Island, rainfall decreased from about 1000 mm/year at the top to about 200 mm/year at the southern coastal area. In the highlands, the sampling points mostly correspond to small springs and seeps, which safely represent local recharge water, although not the samples downslope, which are from large springs. The island has a poorly permeable underlying layer of submarine rocks (basal complex) that crops or subcrops out in the northwestern sector. The most recent lava flows, and even the older ones, are rather pervious and allow the recharge to be conveyed towards the coast, with only a fraction captured by local springs. Based on the altitudinal average chloride deposition rates from Gran Canaria, the probable recharge rate in the island was determined. An average recharge rate of up to 600 mm/year was estimated in the highlands, especially in the central-south area, which is characterized by sparse vegetation and poor soil, and as little as 50 mm/year near the coast.

Estimation of recharge in continental Spain. Research into the applicability of atmospheric chloride balance in the soil was carried out by members of the Geological Survey of Spain (IGME) and the Technical University of Catalonia (UPC), with funding from the two organizations and the Spanish Committee for Science and Technology (CICYT). The results were reported in a doctoral thesis [1] under the guidance of the author. In addition, several papers have been published [2–6] or are in preparation.

The existing Spanish network established to sample atmospheric deposition has been operating in some stations for more than 15 years. Sampling was completed with 2–3 years of data obtained from 17 specially installed rain collectors. These were sampled monthly at strategic points of the peninsular territory and used to supplement earlier data sets as well as results available in the literature. The series was completed by the linear extension of actual measurement days to the total period. Kriging was used to obtain distribution maps of total (wet+dry) chloride deposition, as well as the uncertainty map for these particular sets of series, as shown in Fig. 5.

Chloride exportation with surface water can be mapped and its uncertainty estimated using the adjusted surface water runoff modeled for the Hydrological Plans [22,23] and the Water White Book of Spain [36], with reference to a 10 km × 10 km grid, combined with the stream-water salinity data set of the Ministry of the Environment, which was developed in order to evaluate the contribution of direct runoff (Fig. 6). The Spanish groundwater chemical composition database of the IGME, by identifying small springs and shallow wells, was used to determine the expected average chloride content of recharge water and its uncertainty (Fig. 7).

By combining the regionalized data from Figs. 5, 6, and 7, the spatial distribution map of the estimated virtual recharge rate and its uncertainty was obtained (Fig. 8). A combination of the latter with the rainfall map (Fig. 9) yield the virtual recharge as a fraction of precipitation. The average recharge rate map is a potential (virtual) one, since the results are not directly applicable to areas of low permeability rock outcroppings, in which groundwater renovation is fast, or where there are no permanent groundwater outflows.

Uncertainty, measured through the variation coefficient, was high in some areas, up to 0.4. This results in a relatively poor

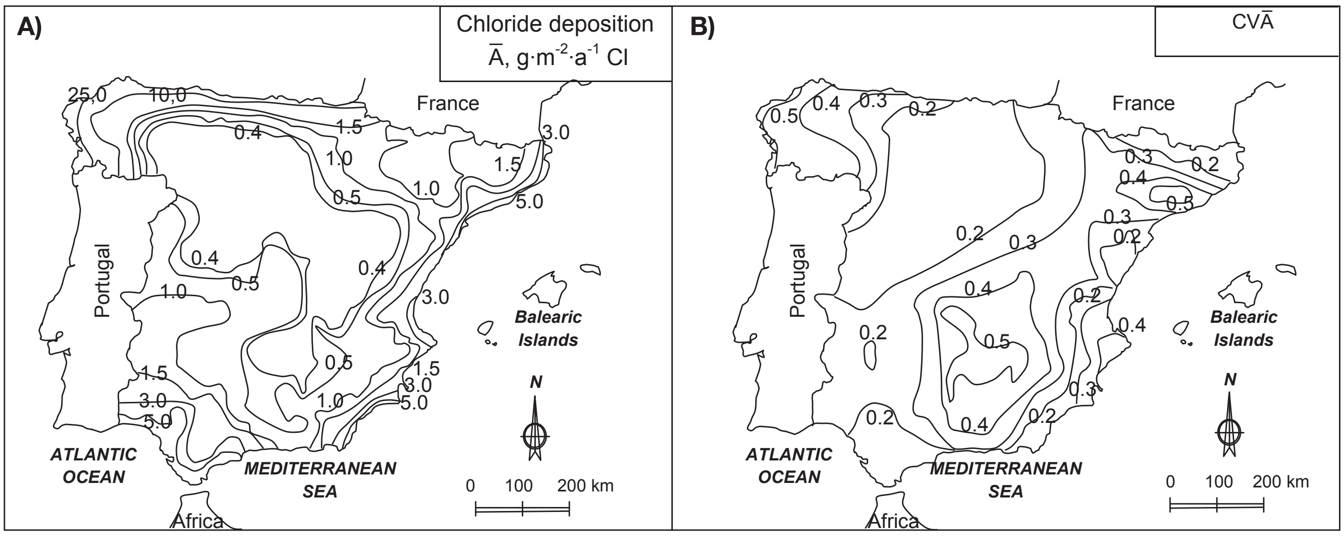

Fig. 5. Preliminary estimation of average atmospheric chloride deposition in conterminous Spain from 10 km × 10 km pixels, as calculated by Alcalá [1]. Contour lines are an approximation, modified from [1,15]. (**A**) Atmospheric deposition (g Cl m^{-2} year^{-1}). (**B**) The coefficient of variation (standard deviation/mean), expressed as a fraction.

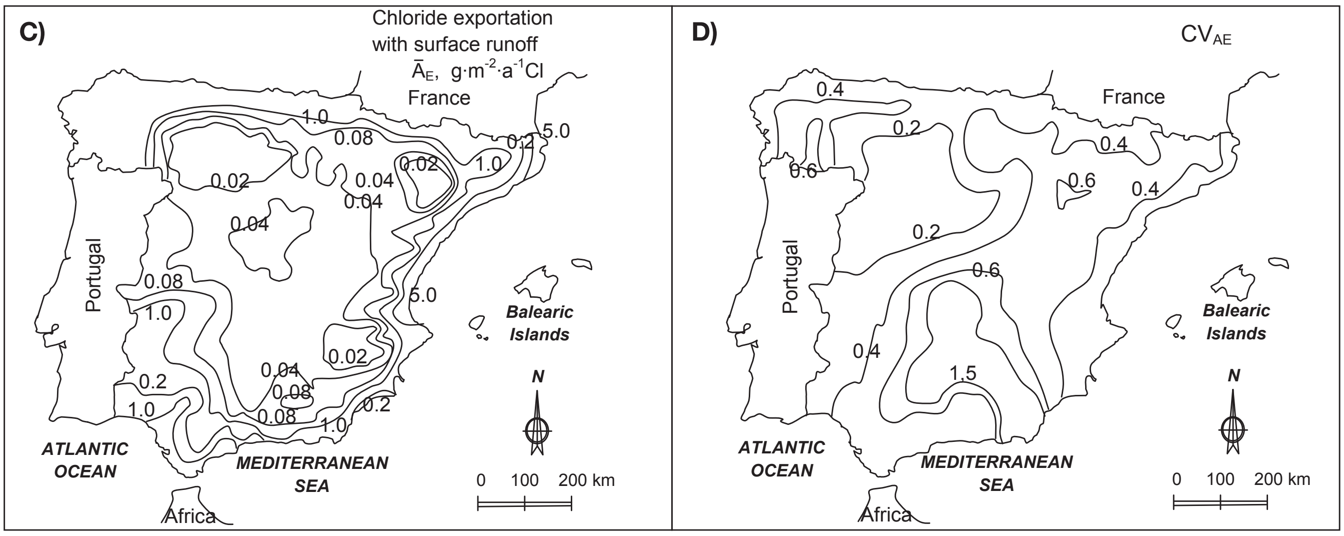

Fig. 6. Preliminary estimation of average exportation of chloride from the land by surface water runoff, in conterminous Spain, deduced from 10 km × 10 km pixels as calculated by [1]. (**A**) Contour lines are an approximation, modified from [1,6], of the chloride exportation value (g Cl m^{-2} year^{-1}). (**B**) The coefficient of variation.

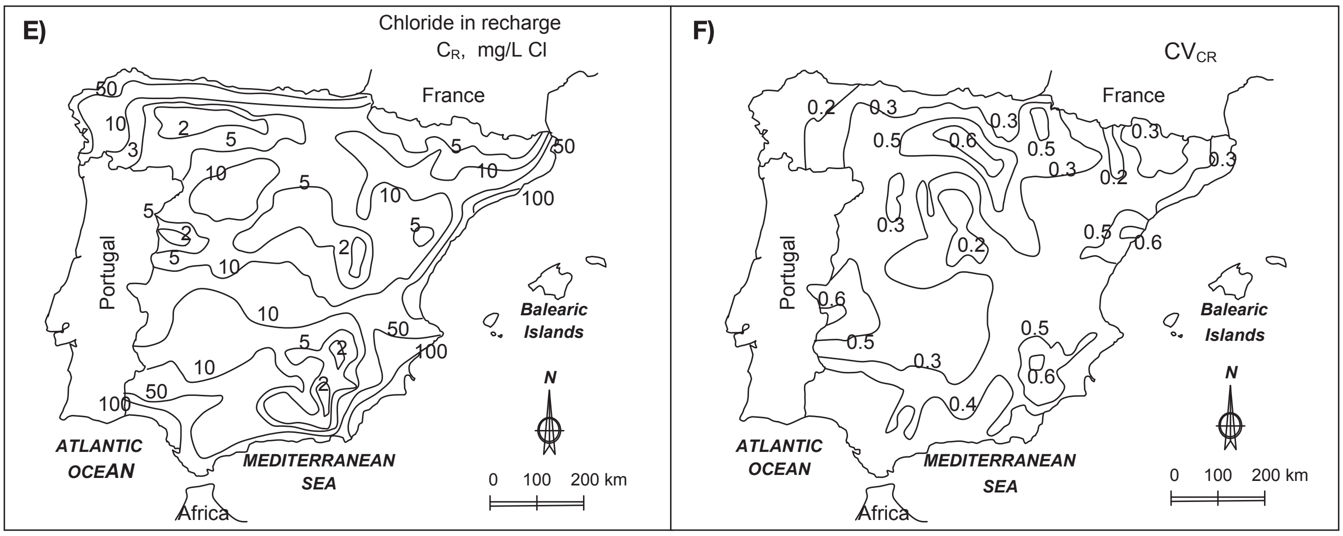

Fig. 7. Preliminary estimation of average chloride content in recharge water in conterminous Spain, deduced from 10 km × 10 km pixels as calculated by Alcalá [1]. (**A**) Contour lines (mg/l Cl) are an approximation, modified from [1,3]. (**B**) The coefficient of variation.

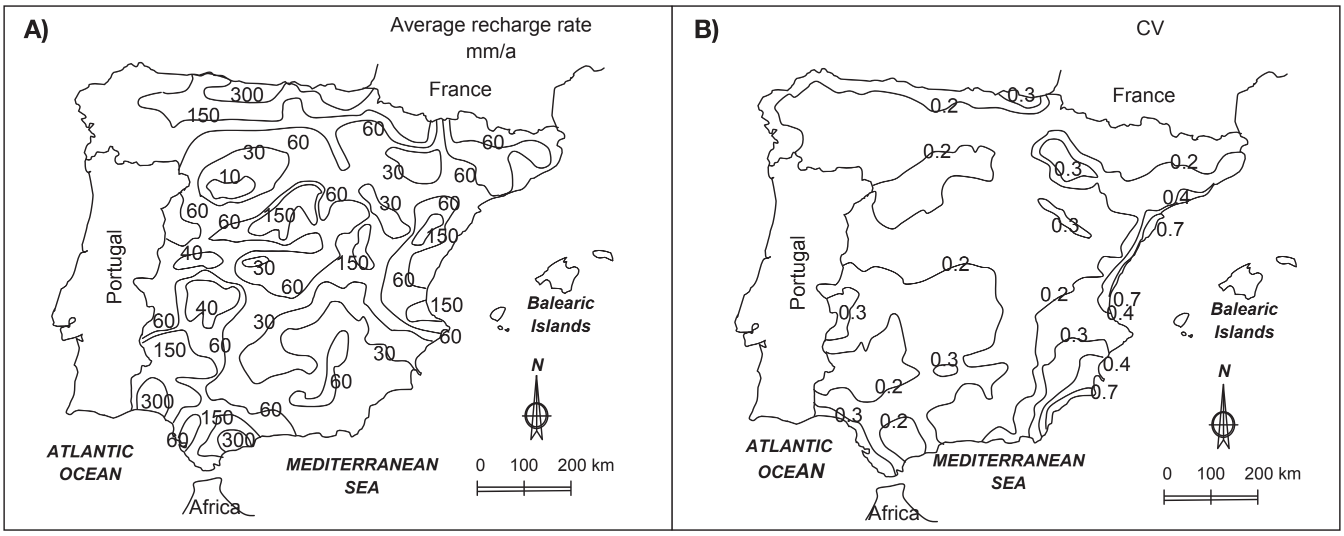

Fig. 8. Preliminary estimation of virtual average recharge rate in conterminous Spain, deduced from 10 km × 10 km pixels, as calculated by Alcalá [1]. (**A**) Contour lines are an approximation of average recharge rates (mm/year), modified from [1,4]. (**B**) The coefficient of variation.

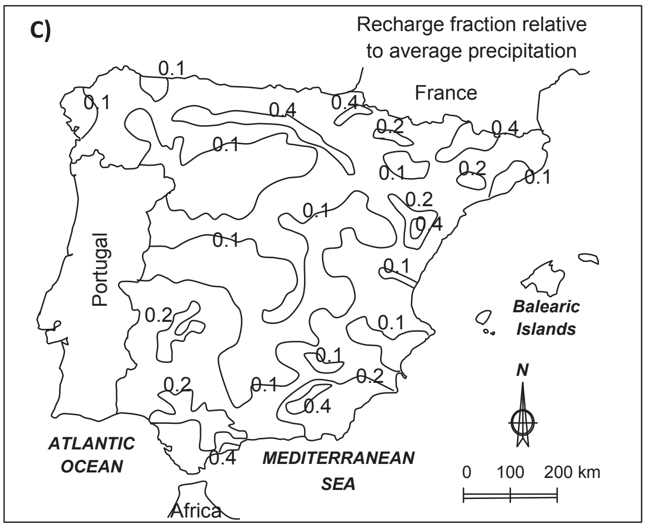

Fig. 9. Preliminary estimation of the fraction of precipitation that is virtual recharge in conterminous Spain, deduced from 10 km × 10 km pixels, as calculated by Alcalá [1].

estimate of the recharge rate based on existing data, although it was not necessarily worse than the estimates obtained with other methods. Improvements are underway to reduce uncertainty.

Conclusions

The atmospheric chloride balance method, used occasionally to estimate the average recharge rate under steady state conditions, is reliable if atmospheric deposition is known (data are rapidly increasing) and the average chloride content can be safely deduced from groundwater surveys. The advantage of this approach lies in its ability to easily provide an estimate of the uncertainty. The method applies to conditions in which recharge is dominantly derived from the diffuse infiltration of precipitation below the root zone and it takes into account the decrease in possible actual recharge due to groundwater evaporation by phreatophytes, or when the water table is very shallow, or rainfall recharge that bypasses the pedologic soil. It does not apply to groundwater discharge areas and when recharge is dominated by unevenly distributed, concentrated infiltration down to the water table, except if mixing in the top water-table layer combines a really average diffuse and concentrated recharge. Long-term steady state conditions through the unsaturated zone are needed. Errors can be introduced due to recent land-use changes and anthropic effects, such as forest or agricultural modifications, or significant artificial additions of chloride to the atmosphere.

Measurements of average atmospheric chloride deposition (wet+dry) require continuous precipitation sampling (daily, per rainfall event, or monthly composite samples) for at least 3–5 complete years, preferably >10 years, although extraordinary occasional events have to be considered to evaluate uncertainty. Recent work by Alcalá and the author is aimed at devising a method to extend short data series to a 10-year reference, including estimates of the uncertainty. In arid areas, especially when the water table is deep, the transit time through the unsaturated zone is often very long, hundreds to thousands of years. Theh a steady state cannot be safely assumed, and the chloride content of the top water-table may not correspond to current recharge.

When groundwater samples come from large catchment-area springs and base-flow streams, long-screened wells, or wells pumping from deep formations, the chloride content does not correspond to local recharge but rather to a mixture of water recharged at upslope outcrops. Therefore, in sloping aquifers with changing precipitation and/or atmospheric deposition, the sampled chloride concentration may be lower–and much lower in arid and semiarid areas–than in local recharge. This means an overestimation of actual recharge when applying a simple atmospheric chloride deposition balance in the soil. The results may even exceed the amount of local rainfall. However, the data may be interpreted by means of a well-mixed model of upslope recharge, which includes the spatial variation when input changes can be constrained. This is a research area that is currently being developed, partly based on previous experience in the interpretation of tritium content.

This article presents several case studies, in much-abbreviated form, with brief comments on the results, their validity, and their application to the entire Spanish peninsular territory. In this case, mapping was based on a 10 km × 10 km grid derived from the regionalization of data by kriging.

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