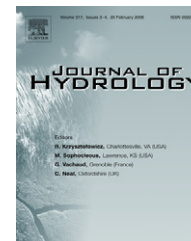




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Using the Cl/Br ratio as a tracer to identify the origin of salinity in aquifers in Spain and Portugal

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Summary A study on the applicability of the Cl/Br molar ratio for identifying the origin of groundwater salinity is presented according to the experience gained in Spain and Portugal. Cl/Br ratios in atmospheric bulk deposition have helped to distinguish groundwater in which Cl derives only from atmospheric sources, from groundwater in which Cl is contributed by endogenous, lithological or anthropogenic sources. Considering the seawater Cl/Br ratio of 655 ± 4 , Cl/Br ratios may be increased up to 1500 in groundwater by the addition of wastewater loaded with NaCl or leaching of solid waste, and decreased to 300 by the use of Br-based pesticides or leaching farm-animal or septic waste. Leaching and dissolution of natural and industrial NaCl, and of gypsum-rich formations containing some NaCl may yield Cl/Br ratios between one thousand and several thousand, although leaching of potassium halides near salt mines produces Cl/Br ratios below the seawater ratio. When Cl content in groundwater is not affected by extreme evaporation (up to halite saturation at $\sim 6.2 \text{ mol L}^{-1}$ of NaCl) and if there are no other Cl sources, recharge by rainfall can be estimated by relating Cl in atmospheric bulk deposition to derived groundwater. The Cl/Br ratio appears to be a good tracer for discriminating non-atmospheric Cl contributions to groundwater, provided chemical analyses are accurate, since its variability is not wide. Data have been collected from different areas of Spain and Portugal and are explained and illustrated by two cases described in detail, the Doñana aquifer in southwest Spain and the Canary Islands, both showing the mixing paths.

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Introduction

Chloride (Cl) and bromide (Br) ions are ubiquitous solutes in all natural water. The first is a major component, the latter a minor one. The major reservoir of water (the ocean) has relatively uniform Cl and Br concentrations and their Cl/Br molar ratio is around 655 ± 4 (Fontes et al., 1986; Whittemore, 1988; Davis et al., 1998; Custodio and Herrera, 2000), although other authors report slightly higher or lower ratios, which may be explained by analytical accuracy and local effects.

Cl and Br ions dissolved in natural water are tracers close to the ideal conservative behaviour due to their hydrophilic character and small ionic size (Custodio and Llamas, 1983; Davis et al., 1998, 2004). Neither of them take part in significant ion exchange reactions at low temperatures, nor are they adsorbed onto mineral surfaces, and as they are so highly soluble, they only form minerals during extreme evaporation conditions when halite starts to precipitate (Fontes and Matray, 1993; Custodio and Herrera, 2000; Herczeg et al., 2001; Cartwright et al., 2006). This means that the physical processes taking place in soil (dilution, evaporation, transpiration, mixtures, etc.) can change the absolute concentrations, but do not significantly modify the Cl/Br ratio of not-too-saline groundwater.

The Cl/Br ratio has been used as a tracer to determine the origin and evolution of groundwater, surface water and brines in oil and gas exploration (Rittenhouse, 1967; Carpenter, 1978; Freeman, 2007), and has become an effective aid in hydrogeological studies of surface and groundwater with low-to-moderate salinity (Whittemore, 1988; Fabryka-Martin et al., 1991; Davis et al., 1998; Vengosh and Hendry, 2001; Cartwright et al., 2006) and the contribution of salinity to lakes and rivers, such as Lake Kinnereth and the Jordan River (Dror et al., 1999; Eastoe et al., 1999; Kolodny et al., 1999; Panno et al., 2006).

The Cl/Br ratio enables the origin of chloride in atmospheric bulk deposition and unpolluted recharge water to be discerned (Fabryka-Martin et al., 1991; Davis et al., 1998; Edmunds, 2001). This makes it possible for the atmospheric chloride contribution to be distinguished from other origins in groundwater and then used to estimate aquifer recharge from precipitation through the chloride mass balance method (Rosenthal, 1987; Wood and Sanford, 1995; Custodio, 1997; Cartwright et al., 2006; Minor et al., 2007; Alcalá and Custodio, 2007, 2008). The Cl/Br ratio can also be helpful in identifying the groundwater flow system when salinity increases due to rock-water interaction (Fontes et al., 1986; Lehmann et al., 1993; Park et al., 2002) or to identify sources of groundwater pollution from surface-derived diffuse anthropogenic compounds (Vengosh and Pankratov, 1998; Hudak, 2003).

However, additional experience in real situations, taking atmospheric input into account, is also needed, either because behaviour has not been well studied or because additional data is required for practical Cl/Br ratio applications. The difficulty in measuring usually low Br concentrations in natural water has limited its application.

In the Iberian Peninsula (Fig. 1), widely diversified geological, orographic and climate conditions (MIMAM, 2000), as well as anthropogenic activity, control the many pro-

cesses modifying the original atmospheric sources of salinity; multiple small aquifers are defined in Spain and Portugal whose sources of salinity are known in many cases and Cl/Br ratios change in a predictable manner. For groundwater recharge estimation, whether at aquifer scale or for the whole Spanish territory, using environmental chemical methods based on the balance of an atmospherically contributed conservative solute, as the chloride ion, requires all the chloride content in shallow groundwater to be strictly atmospheric. Therefore, atmospheric bulk deposition was surveyed at different points throughout the territory (Fig. 1) to find out the regional input of Cl/Br ratios controlling expectable baseline Cl/Br ratios in recharge water with short residence times. For additional information contributed by the Cl/Br ratio, samples were taken from aquifers in Spain and Portugal (Fig. 1) with selected well-known recharge and groundwater flow conditions to observe the potential applicability of the Cl/Br ratio as an effective hydrogeological tracer to discriminate the origin of groundwater salinity.

Basis for interpretation

Global generation and distribution of atmospheric Cl and Br ions and other marine substances from the seawater boundary to the lower stratosphere via rapid deep convection depend on the frequency and intensity of wind and cyclonic activity in terrestrial mid-latitudes (Eriksson, 1960; Duce et al., 1965; Cicerone, 1981). Most cloudy masses entering over Spain and Portugal form in the tropics, and acquire Cl and Br from the ocean for short and long-distance transport, including the generation of longer-lived brominated and chlorinated gases (e.g., Br_3CH_3 , Cl_3CH_3 , etc.) and short-lived halocarbons (e.g., Br_3CH_3 , Br_2CH_2 , Cl_3CH , etc.), which are sources of Cl and Br that can be transported attached to marine aerosols (Yvon-Lewis and Butler, 2002; Solomon et al., 2005; Butler et al., 2007).

Once bulk Cl and Br masses are suspended in the atmosphere they can be carried inland by winds. Atmospheric Cl and Br availability decreases along the wind path with increasing distance from the ocean, resulting in higher Cl and Br deposition rates near the coast than inland (Eriksson, 1960; Davis et al., 1998; Edmunds, 2001; Alcalá and Custodio, 2008). Therefore, coastal rainfall Cl/Br ratios are close to that of seawater. However, there are deviations caused by small differences in Cl and Br chemical behaviour. Both Cl and Br form small amounts of volatile compounds, mostly CH_3Cl and CH_3Br with average Cl/Br ratios of 10–50 (Redeker et al., 2000; Goni et al., 2001), due to organic activity near the sea surface and on the continent (e.g., effect of soil biological activity, burning of vegetation cover) that are incorporated into atmospheric gases and transported by the wind as suspended dust particles. In these processes Br is favoured. This means a small reduction from the Cl/Br ratios on the sea surface, near the coast and a much more intense effect landwards to around 300 or less due to the increasing relative contribution of Br (Fabryka-Martin et al., 1991; Wilkinson et al., 1997; Davis et al., 1998, 2004; Edmunds, 2001; Solomon et al., 2005; Butler et al., 2007), even in “salares” (Risacher et al., 2006).

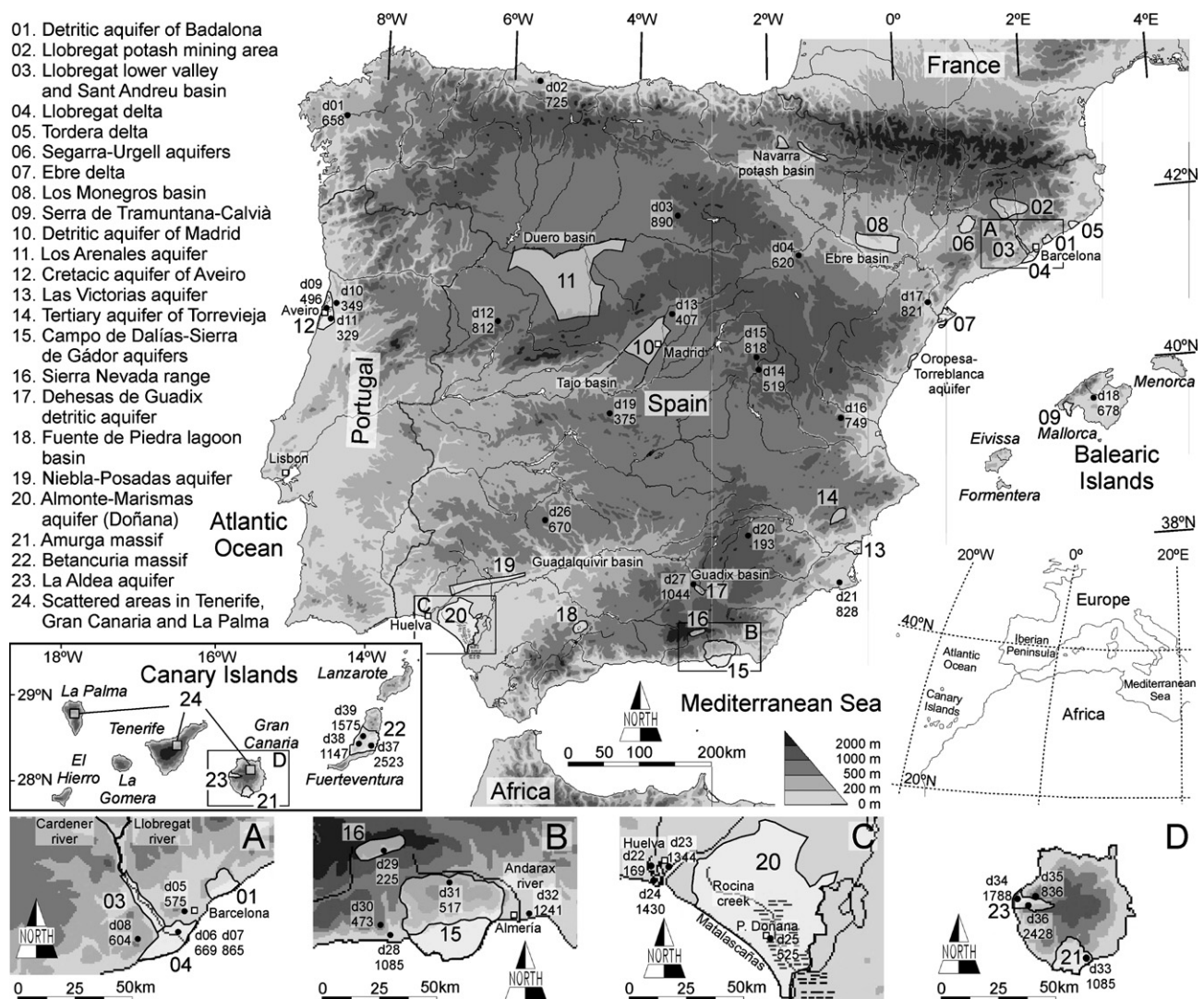


Figure 1 Location of the 24 aquifers sampled in Spain and Portugal and the 39 temporary rainfall sampling stations, including average Cl/Br ratios detailed in Table 1. The main mountain ranges, hydrographic basins and relevant places mentioned in the text are marked. Shadings show altitude ranges from lighter (sea level) to darker (over 2000 m a.s.l.).

This situation may change in windy arid coastal areas, where relatively high Cl/Br ratios up to 1000 have been found in the atmospheric contribution (both dry and wet deposition, and consequently in bulk deposition) in the Canary Islands, and southeast continental Spain (Herrera and Custodio, 2003; Alcalá and Custodio, 2005). A definitive explanation is not available, but this is probably due to chemical fractionation during evaporation of sea droplets generated by the wind on waves rims, thus producing small halite crystals that are transported towards the coast and soon washed down by bulk deposition. Since halite is poor in Br (which remains mostly in the non-evaporated fraction) and goes back to the ocean, the Cl/Br ratio in coastal bulk deposition may increase.

Other factors, such as vegetation cover, proximity to cities and industrial centres, mining facilities, evaporitic rock outcroppings, etc., can contribute locally both natural (e.g., smoke) and anthropogenic (e.g., industrial activity, fuel combustion, etc.) atmospheric dust and organic molecules, in both coastal and inland areas (Yvon-Lewis and But-

ler, 2002). These modify the Cl/Br ratios of local bulk deposition, and even more so during periods of lower incoming marine aerosols linked to rainfall from oceans (Martens et al., 1973; Alcalá and Custodio, 2004, 2005; Alcalá, 2006).

Salinity in atmospheric bulk deposition controls the expectable Cl/Br ratios in groundwater anywhere recharge water has a short residence time in the unsaturated zone, and the contributions of non-atmospherically derived sources of Cl and Br to groundwater are negligible. Normal saline evapoconcentration during recharge does not change Cl/Br ratios in groundwater (Fontes and Matray, 1993; Davis et al., 1998; Edmunds, 2001).

The main natural and anthropogenic processes modifying the original groundwater chemical composition derived from atmospheric input are known and have been relatively well studied. Since the Cl and Br ions dissolved in groundwater maintain a reasonable record of the bulk rainfall contribution and its Cl/Br ratio, it is possible to use the Cl/Br ratio to find out the local origin of salinity with a regional spatial distribution of Cl/Br ratios in meteoric water. The composi-

tion of seawater is used as a reference to compare differences in water and infer behaviour, mixing patterns and solute contribution, as described below.

Evaporation of seawater does not change the Cl/Br ratio up the point when halite starts to precipitate at about 6.2 mol L^{-1} NaCl concentration. Precipitated halite is very poor in Br, especially in the early phases, since Br is not easily included in the crystalline network. The halite Cl/Br molar ratio may be up to 40,000 (Herrmann, 1972). Gypsum precipitated in this early evaporation may contain halite of this type (Ayora et al., 1995), but also residual brine trapped in the rock with a ratio close to or higher than seawater. As Cl precipitates, Br is held in the solution, and its Cl/Br ratio decreases conspicuously, from molar ratios of about 655 down to about 70 in the residual brine (McCaffrey et al., 1987; Fontes and Matray, 1993; Vengosh et al., 1998; Custodio and Herrera, 2000; Taberner et al., 2000; Cartwright et al., 2004). During the last stages of halide crystallization from brine, at the time K replaces Na, a fraction of Br replaces Cl in precipitated minerals and the Cl/Br molar ratio starts falling to 800, and even lower in precipitated potash halides such as sylvite (KCl) and carnalite ($\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$), while in the residual brine, it drops to less than 40 (Taberner et al., 2000). In oil-field seawater-derived brines, Cl/Br ratios are typically in the range of 100–300, although they can vary widely (Rittenhouse, 1967; Carpenter, 1978; Vengosh et al., 1998).

Common solar salt production techniques employing large open evaporation ponds from saline lake-water or seawater, industrial procedures, and natural and mining brines result in halite Cl/Br ratios between 5000 and 40,000.

Halite dissolution produces a rapid increase in Cl/Br ratios in water with increasing Cl concentrations (Kloppmann et al., 2001). Use of NaCl in food preparation for humans and cattle contributes Cl to urban wastewater, raising the Cl/Br ratios up to >1500 (Vengosh and Pankratov, 1998). In general, wastewater tends to have a high Cl/Br ratio due to the use of halite in the home and many commercial and industrial processes, but not always, because of many other influences, as shown in Vengosh et al. (2005).

The dissolution of Br-rich evaporitic salts from the final stages of seawater evaporation (e.g., sylvite, carnalite) may produce low Cl/Br molar ratios, less than 100. However, this only occurs in mining areas or where these minerals are especially abundant, such as in the mid-Llobregat basin, Barcelona (Ayora et al., 1995; Taberner et al., 2000) or when potash salts are used as an agrochemical fertiliser. The dissolution of Cl-bearing contaminants such as chlorinated solvents (or their degradation products), or salt used for road de-icing may also increase the Cl/Br ratios, while contamination by volatile hydrocarbons from combustion of automotive fuels or Br-based halocarbons, mainly ethyl dibromide, and methyl bromide used as soil disinfectants and pesticides to control nematodes and weeds in agriculture, may reduce the Cl/Br ratio to below 300, and sometimes under 50 (Davis et al., 1998). The use of some of these compounds is currently forbidden in many countries — including Spain — due to their toxicity, but the effect of past applications in soil and groundwater may be long-lasting, even though in many areas they have been replaced by other agrochemicals (Bello et al., 2001; De Cal et al., 2005).

Volcanism is a source of halide emissions to the atmosphere and directly into groundwater. Magma contains moderate quantities of Cl and Br that are released as it cools and solidifies, both as gases (HCl, HBr, Br-oxides) or dissolved in exolved water (vapour or liquid). Cl/Br ratios of halides in magma and resulting rocks vary from much lower (2 after Bureau and Métrich, 2003) to higher than the seawater ratio, and are variable in exolved gases, about 1500 in gases from the recent eruption of Mt. St. Helens (Fruchter et al., 1980), and about 40 in air from active Mt. Etna. In highly saline lakes receiving volcanic gases and "solfaratas" in Indonesia, the Cl/Br ratio is 255 (Delmelle and Bernard, 1994), and 70–1600 in Indonesian/Java volcanoes and about 225 in recent volcanic eruptions on Montserrat Island (Bobrowski et al., 2003). In general Cl is released more easily than Br (Aiuppa et al., 2005; Schaefer and Fegley, 2005). Br concentrations are negatively correlated with pressure in H_2O -saturated silicic melts (as volcanic glasses) and directly correlated with SO_2 released (Bureau and Métrich, 2003). The tendency for mineral hydration during degassing increases Cl/Br ratios up to 1000 in water.

Both Cl and Br ions, atmospherically-contributed or premeditatedly added, can be adsorbed in soil organic matter to some extent (Gerritse and George, 1988; Öberg and Sandén, 2005), thus changing the Cl/Br ratio in water, but this barely affects recharge water as a steady state is easily achieved. However, changes in land use may induce strong release of Br when forest is cleared and organic matter in soil and terrain is oxidized (e.g., by ploughing), thus reducing the Cl/Br ratio. Intensive organic retention of Cl was reported by Hudak (2003) from farm-animal waste leachates, yielding Cl/Br ratios around 200–350.

Cl/Br ratios allow identifying groundwater whose salinity derives from atmospheric sources, but this groundwater composition may be changed by mixing with another type of water or by adding a solid solute with a given Cl/Br ratio to it. A basic formulation for quantifying these common processes is presented in Appendix A. Some scenarios of water mixtures and solid solute additions to water evolving differently have been considered (Fig. 2). The result is commonly shown by plotting the Cl/Br ratio vs. Cl.

Analytical methods

The Cl/Br ratio, also indicated as R , (given this way to yield values greater than 1) is expressed here as the molar ratio, which is 2.253 times the weight ratio.

Accurate measurement of the chloride ion concentration does not involve any special difficulty, except at $<1 \text{ mg L}^{-1}$ concentrations, which is not common in groundwater, but does occur in continental rainwater. In freshwater, the bromide ion appears most often at $<1 \text{ mg L}^{-1}$ concentrations, and frequently at $<10 \mu\text{g L}^{-1}$, which means that improved analytical methods are required.

Common spectrometric analytical methods for Br determination do not provide the required accuracy, while the ion-selective electrode method has variable interference at the expected Cl/Br ratios. The colorimetric method, in which the evolution of a controlled reaction is halted at a precise time, and high performance liquid (anionic) chromatography (HPLC) are accurate enough for Br determination

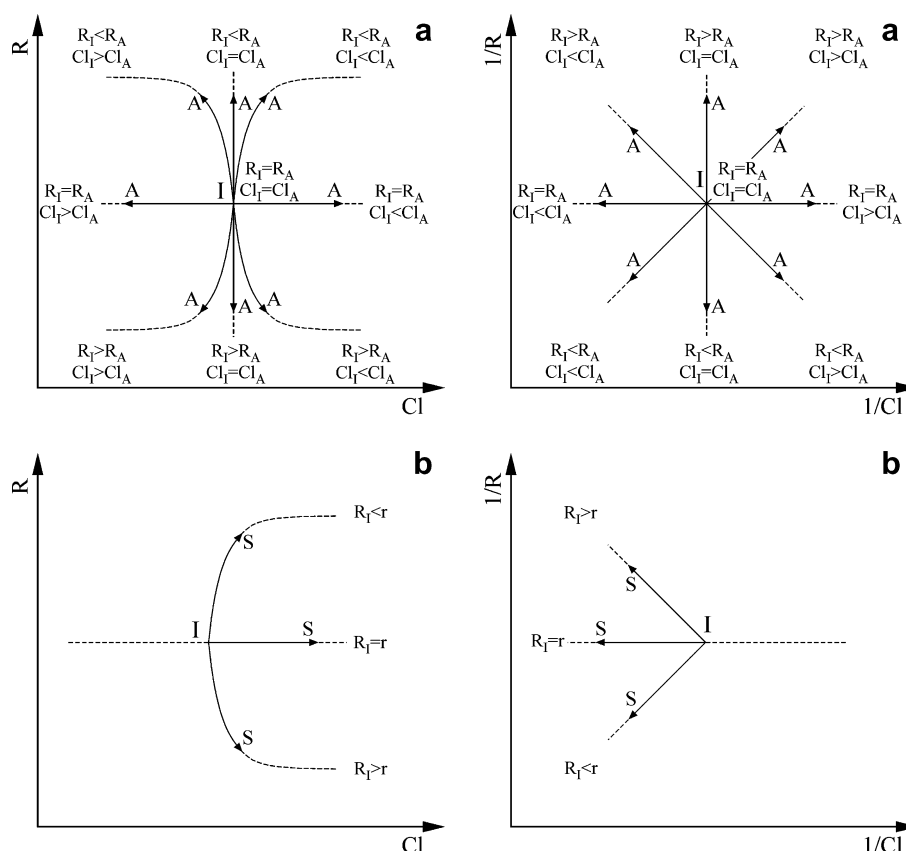


Figure 2 (a) Mixing scenarios for real freshwater incorporating a fraction of more or less saline water with $R_I < R_A$, $R_I = R_A$ and $R_I > R_A$, where R is the Cl/Br molar ratio, and I and A are initial and added water denoted as subindices. (b) Freshwater with a given R dissolving an amount of solid solute S per unit water volume, where $r = cl/br$ (molar concentration of Cl and Br in the solid), and $R_I < r$, $R_I = r$ and $R_I > r$. Mixing of end-members are plotted in an R vs. Cl follow a curve with an unchanging slope and in a $1/R$ vs. $1/Cl$ linear plot. Axes remain linear.

in natural water and rainfall, as they allow efficient separation of Cl and Br peaks and accurate measurement of Br at $<5 \mu\text{g L}^{-1}$ concentrations (Davis et al., 2004), with a reported detection limit of $1 \mu\text{g L}^{-1}$. In no case is there interference between the Br peak and the nearby NO_3 peak. Br measurement uncertainty is also low with the neutron activation method (Koglin, 1984), but this method was not employed here.

Cl and Br concentrations were analysed by the Geological Survey of Spain (IGME) Laboratory following the EPA 300 1A method (Hautman and Munch, 1997) on filtered unacidified samples. A DIONEX 600[®] high-performance liquid (anionic) chromatograph was used. Due to large differences in major and minor component concentrations in a sample, they have to be analyzed in two different chromatographic runs using either different sensitivity settings on the detector or different sample dilutions. A complete chromatographic run lasts 17 min. An IonPac AS9-HC[®] analytical column was used in combination with the AG9-HC[®] guard column. The eluent is Na_2CO_3 9 mM at a flow rate of 1.25 mL. The detection system is suppressed electrical conductivity. The injection loop capacity is typically 25–250 μL . For low concentrations of analytes, larger injection loops can be used to increase sensitivity, up to 2500 μL . The dilution is calculated for the best concentration for efficient measurement.

The analytical sensitivity to separate Cl and Br peaks was developed from 2001 to 2006 and was progressively corrected using certified Aquacheck Programme calibration standards plus a blank. The calibration standards were analysed during the run to monitor drift. For a Br between about 20 and $90 \mu\text{g L}^{-1}$ and a Cl between about 5 and 100mg L^{-1} for weakly mineralized natural water, including rainwater, the IGME and Aquacheck certified intercalibration means differ by $-0.04 \pm 4.46\%$ for Br and $-0.92 \pm 5.19\%$ for Cl.

Overall analytical accuracy, given as relative error through the coefficient of variation ($\text{CV} = \text{standard deviation} (1\sigma)/\text{mean}$), was based on replicate analyses of internal standards and samples within and between runs (Custodio and Alcalá, 2004; Vázquez and de la Fuente, 2007). Aliquots of groundwater and rainwater samples with Cl/Br ratios close to that of seawater (655) were analysed independently to ensure the accuracy of both anion assessments. The error for Cl concentrations over 0.5mg L^{-1} was around $\pm 3\%$; for Br concentrations over $1 \mu\text{g L}^{-1}$ it was around $\pm 8\%$ improving to $\pm 3\%$ for Br concentrations over $5 \mu\text{g L}^{-1}$, resulting in an error of around $\pm 6\%$ for water in which the Cl/Br ratio is close to seawater. The error is less than $\pm 8\%$ for water with low Br concentration and Cl/Br ratios over 1500 (e.g., water including natural or industrial halite) and $\pm 4\%$ for water with

high Br concentrations and Cl/Br ratios below 300 (e.g., water including anthropogenic Br-based compounds). These results are similar to those reported by Stevens (1990) and Dror et al. (1999), and slightly better than reported by Vengosh and Hendry (2001) and Cartwright et al. (2006), who both used ion chromatography in moderately saline samples.

Results

A study on the applicability of the Cl/Br ratio to know the origin of groundwater and rainwater salinity in Spain and Portugal was carried out from 1998 to 2005. First criteria were needed for selecting groundwater samples with salinity derived from atmospheric sources in order to estimate average recharge by rainfall to Spanish aquifers through the chloride mass balance method (Alcalá and Custodio, 2007, 2008).

An atmospheric deposition sampling network was set up to determine the saline input to land at 39 sites in Spain and Portugal (Alcalá and Custodio, 2008; Fig. 1 and Table 1), by collecting atmospheric bulk deposition (in open collectors), wet deposition (saline content in rainwater measured by means of samplers that only open when there is rain), and dry deposition (the saline content directly deposited on the land surface in the form of airborne dust or atmospheric aerosols). The sampling network was designed to acquire data on the Cl/Br ratios in bulk deposition under different atmospheric conditions, covering locations at different altitudes and distances from the coast. Cl/Br ratios around or higher than seawater were found at unpolluted coastal fringes of the Atlantic Ocean and the Mediterranean Sea, decreasing to less than 200 in the centre of the Iberian Peninsula (e.g., stations d01, d02, d18; Fig. 1 and Table 1). Cl/Br ratios up to 1000 and occasionally up to 2000 were found at semiarid to arid coastal fringes in the southeast Iberian Peninsula and southern Canary Islands (e.g., stations d28, d32–d39; Fig. 1 and Table 1), where there is a strong dry deposition component of up to 50% of total deposition (Alcalá and Custodio, 2008).

A large number of natural and anthropogenic sources of salinity in Spain and Portugal modify the groundwater Cl/Br ratios in rainfall. Some stations located in the major Spanish River basins (Ebre, Duero, Tajo) and other minor basins such as Guadix (Granada), where there are outcrops of sedimentary Neogene lithology, including gypsum formations. Lithology contributes a natural source of salinity to atmospheric bulk deposition through wind-blown halite raising the Cl/Br ratios up to 800 and occasionally up to 1000 (e.g., stations d03, d12, d15, d17, d27; Fig. 1 and Table 1).

Other stations were installed in polluted urban and industrial coastal and inland areas. Bulk deposition in the polluted urban and industrial coastal areas around Barcelona (stations d05–d07; Fig. 1), Aveiro (stations d09–d11; Fig. 1), in Doñana (downwind Huelva) (stations d22–d23; Fig. 1), and in intensive agricultural exploitation under greenhouses in Campo de Dalías (Almería), shows Cl/Br ratios below the seawater ratio (station d30; Fig. 1). Combustion of automotive and industrial fuels, burning plastic and garbage, etc., contribute additional sources of salinity to marine aerosols with more Br than Cl (Martens et al., 1973;

Alcalá and Custodio, 2004). The cause may be the release of Br-rich volatile compounds used as soil disinfectants and pesticides in intensive agriculture, or contributed by hydrocarbon processing plants and combustion facilities (Querol et al., 2002; De Cal et al., 2005).

From previous experience in Spain and studies dealing with hydrogeology, geochemistry and isotopic data (Custodio and Herrera, 2000; Alcalá and Custodio, 2005; and references included in Table 2), 22 aquifers in continental Spain and the Balearic Islands, the Cretacic coastal aquifer in Aveiro (Portugal), and scattered areas in the Canary Islands, were selected for surface and groundwater sampling (Fig. 1). Salinity described in these surveys may be divided into the following six main processes contributing to salinity (Table 2): (i) current and relic seawater contributions to freshwater (including seawater-derived brines), (ii) recharge water produced under different climatic, orographic and environmental conditions, (iii) leaching of natural evaporites contributing NaCl, (iv) endogenous degassing in volcanic areas, (v) urban, industrial and anthropogenic NaCl and Br-based compounds, and (vi) leaching of potassium halides near potash mines. Moreover, other significant subprocesses were defined to further specify these main sources of salinity.

The search for information was thorough but not exhaustive. Further information may be found in Giménez and Morrell (1997) on marine intrusion in the Oropesa-Torreblanca aquifer (Castelló de la Plana) (Fig. 1), where background Cl/Br ratios are about 500 and even lower, and Sanchez-Martos et al. (2002), who provide information on the semi-arid Andarax alluvial aquifer (Almería) (Fig. 1).

The Cl/Br ratio was studied in data pooled from 600 samples taken for this survey and from previous studies. The original relative amount of freshwater mixing with other water or dissolving a solid solute controls the magnitude of each saline process observed in each aquifer and their range of variation. Although the magnitude is similar in all the aquifers, there are extreme cases representing saline end-members. Table 2 summarizes the mean Cl/Br ratio and the estimated standard deviation (1σ) for each aquifer salinity process.

Due to the large amount of data generated, only two selected aquifer areas are described below by way of example to show the methodology and data treatment: the Almonte-Marismas aquifer (Doñana), and selected samples from wells, springs and galleries in Gran Canaria, Tenerife, La Palma and Fuerteventura (Canary Islands). Alcalá (2006) provides a more detailed discussion of Cl concentrations and Cl/Br ratios in each sample, along with a short description of the main hydrogeological properties (type and rate of recharge, groundwater flow system, hydrogeochemistry, etc.) of each aquifer at the website [<http://www.tesis-enxarxa.net/TDX-0607106-104930/>].

Almonte-Marismas aquifer (Doñana)

The Almonte-Marismas aquifer system, also known as Doñana aquifer (aquifer 20; Fig. 1), is a Plio-Quaternary detritic formation with an impermeable base consisting of Pliocene to Miocene sandy clays and marls. Towards the north and west, this coastal plain consists of Quaternary fluvio-marine

Table 1 Location, sampling period, average Cl/Br molar ratio, yearly atmospheric bulk Cl deposition rate (A) and average Cl content from temporary rainfall sampling stations installed in Spain and Portugal

Station	Code	Coordinates	Elevation (m a.s.l.)	Sampling period		n	Cl/Br molar	A (g m ⁻² year ⁻¹)	Cl (mg L ⁻¹)	Type of deposition
				From	To					
Santiago	d01	42°52'N 8°31'W	285	19 March 2001	10 September 2002	540	658	3.9	3.0	Bulk
Quintana	d02	43°22'N 5°31'W	377	30 March 2001	02 August 2002	490	725	2.8	3.0	Bulk
Huerta del Rey	d03	41°50'N 3°20'W	1007	29 March 2001	19 August 2002	508	890	0.4	0.8	Bulk
Sierra de Vicort	d04	41°22'N 1°29'W	1383	04 April 2001	02 August 2002	485	620	0.3	0.7	Bulk
Barcelona	d05	41°23'N 2°06'E	125	01 March 1999	04 April 2003	1495	575	4.0	6.1	Bulk
El Prat de Llobregat	d06	41°15'N 2°05'E	20	15 September 1903	09 September 2005	725	669	7.5	15.1	Bulk
El Prat de Llobregat	d07	41°15'N 2°05'E	20	10 September 2003	31 July 2004	325	865	1.7	20.6	Dry
Bruguers	d08	41°19'N 1°57'E	277	17 February 2005	05 February 2006	353	604	2.7	3.3	Bulk
Aveiro	d09	40°38'N 8°39'W	3	01 October 1985	01 October 1989	1461	496	4.8	5.3	Bulk
Albergaria a Velha	d10	40°41'N 8°28'W	131	01 October 1985	01 October 1989	1461	349	4.6	3.6	Bulk
Oliveira do Bairro	d11	40°31'N 8°29'W	60	01 October 1985	01 October 1989	1461	329	3.6	3.4	Bulk
La Bastida	d12	40°34'N 6°03'W	1114	29 March 2001	06 September 2002	526	812	0.4	0.7	Bulk
El Casar	d13	40°42'N 3°25'W	831	22 May 2001	07 December 2002	564	407	0.4	0.9	Bulk
Cuenca	d14	40°03'N 2°07'W	998	03 April 2001	01 August 2002	485	519	0.2	0.5	Bulk
Sotos	d15	40°12'N 2°09'W	991	01 March 2001	06 March 2001	5	818	0.3	5.5	Wet
Siete Aguas	d16	39°29'N 0°54'W	799	30 March 2001	04 September 2002	523	749	1.0	1.5	Bulk
Roquetes	d17	40°49'N 0°30'W	50	16 October 2002	04 November 2003	384	821	1.1	1.6	Bulk
Sta. M. del Camí	d18	39°38'N 2°45'E	230	05 April 2001	02 August 2002	484	678	0.8	5.2	Bulk
San Pablo	d19	39°33'N 4°21'W	917	10 October 2002	10 November 2003	396	375	0.6	0.5	Bulk
Taibilla	d20	38°08'N 2°18'W	940	08 December 2004	02 January 2005	25	193	0.4	0.8	Bulk
Cartagena	d21	37°36'N 0°58'W	55	15 October 2004	02 November 2004	18	828	5.8	9.2	Bulk
Chemical Huelva	d22	37°17'N 6°59'W	10	14 October 1999	07 September 2000	329	169	0.7	5.9	Dry
Phosphate Huelva	d23	37°13'N 6°56'W	10	20 July 1999	23 December 2000	522	1344	1.8	74.5	Dry
Huelva coast	d24	37°13'N 7°01'W	5	23 October 1999	29 December 2000	433	1430	2.2	62.8	Dry
Doñana	d25	36°59'N 6°26'W	5	30 November 2000	27 December 2001	392	525	1.2	4.1	Bulk
Peñarroya	d26	38°18'N 5°16'W	577	30 March 2001	30 September 2002	549	670	0.5	0.8	Bulk
Dehesas de Guadix	d27	37°35'N 3°06'W	674	30 January 2001	29 August 2002	576	1044	1.4	3.1	Bulk
Adra	d28	36°45'N 3°00'W	25	15 December 2002	15 March 2004	456	1085	5.1	15.8	Bulk
Las Yeguas	d29	37°05'N 3°01'W	1971	15 March 2002	01 April 2002	17	225	0.3	1.0	Bulk
Guainos	d30	36°45'N 3°04'W	85	08 June 2004	21 July 2004	43	473	2.1	5.7	Bulk
Ohanes	d31	37°03'N 2°45'W	1020	03 March 2001	01 May 2001	59	517	0.8	2.1	Bulk
University of Almería	d32	36°50'N 2°23'W	20	04 March 2001	30 August 2002	544	1241	5.3	9.8	Bulk
Morro Besudo	d33	27°46'N 15°31'W	50	05 December 2001	14 February 2002	71	1085	1.1	19.3	Bulk
Depuradora	d34	28°00'N 15°48'W	14	31 October 2000	03 May 2002	549	1788	25.1	348.8	Bulk
Tabladas	d35	27°59'N 15°46'W	188	31 October 2000	30 April 2001	181	836	6.2	51.0	Bulk
Artéjvez	d36	27°58'N 15°47'W	338	31 October 2000	03 May 2002	549	2428	2.9	30.6	Bulk
Pozo Negro	d37	28°19'N 13°56'W	90	02 December 1999	06 December 1999	4	2523	3.8	11.7	Bulk
Pájara	d38	28°20'N 14°06'W	190	02 December 1999	06 December 1999	4	1147	10.6	18.8	Bulk
Morro Velosa	d39	28°26'N 14°02'W	680	02 December 1999	06 December 1999	4	1575	7.4	31.5	Bulk

n is the number of days with a continuous precipitation record analysed.

Table 2 Average Cl/Br molar ratio and standard deviation (1σ) found for the main salinity processes and subprocesses in 24 aquifers in Spain and Portugal

Main processes of salinity acquisition	Sub-processes	Aquifers and references																								
		01. Detritic aquifer of Badalona (Montes and Vázquez-Suné, 2005)	02. Llobregat potash mining area (Soler et al., 2002)	03. Llobregat lower valley and Sant Andreu basin (Custodio, 1994)	04. Llobregat delta (Iribar et al., 1997)	05. Tordera delta (Falgàs et al., 2004)	06. Segarra-Urgell aquifers (Pascual and Bayó, 1991)	07. Ebre delta (Bayó et al., 1997)	08. Los Monegros basin (Castañeda and García-Vera, 2008)	09. Serra de Tramuntana-Calvià (López and Mateos, 2003)	10. Detritic aquifer of Madrid (Fernández-Uría et al., 1985)	11. Los Arenales aquifer (Ceballos-Barbancho et al., 2008)	12. Creusic aquifer of Aveiro (Condoso de Melo et al., 2001)	13. Las Victorias aquifer (ITGE-DGOHCA, 1999)	14. Tertiary aquifer of Torrevieja (ITGE, 1994)	15. Campo de Dalias-Sierra de Gádor aquifers (Contreras et al., 2008)	16. Sierra Nevada range (Gisbert et al., 1998)	17. Dehesas de Guadix detritic aquifer (Moreno et al., 2000)	18. Fuente de Piedra lagoon basin (Kohlháň et al., 2008)	19. Niebla-Posadas aquifer (Manzano et al., 2001b)	20. Almonte-Marismas aquifer (Custodio et al., 2001)	21. Anurga massif (Custodio, 1992)	22. Betancuria massif (Herrera and Custodio, 2003)	23. La Aldea aquifer (Cabrera et al., 2000)	24. Tenerife, Gran Canaria, La Palma wells, springs and galleries (Seeger, 1991)	
1. Seawater origin	1.a. Seawater				n=1 646															n=1 586						
	1.b. Seawater intrusion	n=2 686±2			n=12 764±66	n=12 641±20						n=8 656±59	n=3 647±28	n=4 652±20						n=7 639±24			n=22 747±74		n=66 623±80	
	1.c. Seawater brines							n=2 641±32												n=1 660	n=5 619±78			n=2 741±9		
2. Recharge waters	2.a. Coastal areas	n=2 656±16		n=2 664±7	n=3 623±19							n=24 643±43		n=2 595±37							n=10 641±50			n=10 759±50		
	2.b. Inland areas						n=5 602±68		n=2 564±77	n=46 357±64	n=7 541±36							n=1 440	n=10 565±148							
	2.c. High altitude / continental						n=1 396								n=2 509±11	n=1 225			n=7 339±83					n=20 484±93		
	2.d. Coastal arid climate														n=2 509±11	n=1 225			n=7 339±83				n=4 700±14	n=20 831±136	n=1 1064	n=6 981±169
	2.e. Coastal polluted areas			n=4 449±34									n=17 471±104								n=11 487±48					
3. Natural evaporites	3.a. Leaching of halite		n=13 5181±1521						n=5 4734±941		n=1 4611										n=1 5556					
	3.b. Leaching of gypsum containing halite		n=1 7447				n=10 1335±957		n=11 1447±339	n=1 946	n=11 590±131	n=2 720±46	n=16 786±62	n=1 2734				n=9 1728±295								
4. Volcanic origin																						n=3 828±15			n=6 1046±425	
5. Urban, industrial and anthropogenic origin	5.a. Use of Br-based pesticides in agriculture												n=8 402±128								n=4 316±68		n=6 718±74	n=2 275±146	n=7 296±35	
	5.b. Leaching of industrial halite	n=1 6775										n=1 4743														
	5.c. Leaching of garbage and solid waste			n=8 845±30	n=4 803±91	n=2 672±82							n=13 756±62													
	5.d. Leaching of urban wastewater	n=7 1033±179		n=7 952±89	n=5 1380±366	n=3 1207±45	n=4 1658±692				n=14 883±310	n=1 1184	n=7 1063±217			n=1 1500	n=2 938±6		n=1 1012							
	5.e. Leaching of septic waste																n=2 463±78									
6. Leaching of potassium halides around salt mines	6.a. Leaching of carnalite		n=2 508±41																							
	6.b. Leaching of sylvite		n=3 355±32																							
	6.c. Effluent for flotation dumps		n=7 577±82	n=14 775±38																						

Columns show the aquifers selected and a reference guide describing their main hydrogeological properties (aquifer location and code are shown in Fig. 1). n is the number of samples taken from each aquifer for each process and subprocess.

and aeolian sand formations which make up the main unconfined regional rainfall recharge area. Towards the south-east, detritic marine and fluvio-deltaic facies develop (Salvany and Custodio, 1995). The fluvio-deltaic facies are confined under estuarine clayey silts and are topped by tidal and fluvial marsh deposits in which there is now a large temporal marsh, which can include saline and hypersaline relic seawater in more distal deltaic-marine deposits (Custodio et al., 2001; Manzano et al., 2001a). The coastal fringe is occupied by active Holocene dune belt systems, containing phreatic lagoons occupying depressions at the inner boundary of the dune belts in a gently rolling landscape.

Precipitation comes from the Atlantic Ocean and averages 550 mm year^{-1} at the Palacio de Doñana (5 m a.s.l.). Rainwater is the only source of diffuse recharge. A small river base flow, springs, oozings at the coast and in the marsh, and pumping for urban and irrigation supply along its outer boundary are the main discharges (ITGE, 1992; Suso and Llamas, 1993; Custodio and Palancar, 1995). Doñana has important groundwater-dependent wetlands (Custodio, 2000; Manzano et al., 2001a).

Hydrogeological, hydrochemical and isotopic knowledge gained during recent decades (Custodio et al., 2001; Manzano et al., 2001a) has shown the main sources of natural salinity in the area. These studies also provide information about anthropogenic processes modifying current or natural relic sources of salinity. Forty samples were taken of water affected by natural and anthropogenic sources of salinity, some of them from the same sampling point on different dates (Table 2). Every sample was classified according to the origin of its salinity into six groups (Fig. 3): (i) rainwater, (ii) unpolluted old phreatic water, (iii) recent phreatic water, (iv) polluted phreatic water, (v) saline and hypersaline relic seawater, and (vi) water affected by wastewater.

The Cl/Br ratios in rainwater may be divided into two groups (end-members) with intermediate situations (Fig. 3). Cl/Br ratios are similar to seawater during prolonged winter and spring rainfall events coming from the Atlantic Ocean; this dataset includes typically marine ionic ratios. Prolonged dry periods during summer and autumn followed by short, intense rainfall events produce Cl/Br ratios below that of seawater. This dataset sometimes has SO_4 and NO_3 content as high as 15 and 10 mg L^{-1} , respectively. Atmospheric bulk deposition in the Doñana area may include a local contribution from past use of volatile Br-based pesticides in intensive agriculture (e.g., disinfection of sandy soils with methyl-bromide) and pollutants from Huelva's chemical factories to the west (Querol et al., 2002), where preliminary studies on atmospheric dry deposition show Cl/Br ratios between 200 and 500 (stations d22–d23; Fig. 1 and Table 1). Dry deposition at the coastline shows Cl/Br ratios up to 1000 (station d24; Fig. 1 and Table 1).

There are several types of salinity and Cl/Br ratio ranges in groundwater. End-member samples explain and quantify water mixtures, unaffected freshwater, or the addition of solid solutes. Four of these processes have been studied and plotted (Fig. 3).

Curve I in Fig. 3 is a horizontal evaporation line affecting unpolluted rainwater and producing unpolluted old phreatic water, i.e., groundwater with a relatively long residence time (tens of years for deep groundwater), having Cl/Br ratios between 600 and 700 (Table 2) for Cl between 15 and

30 mg L^{-1} . The range of Cl/Br ratios is similar to that of seawater and may be explained by decades of airborne marine aerosols from the nearby coast.

Curve II is a horizontal mixing line of unpolluted old phreatic water with salinity derived from unpolluted marine aerosols, with saline and hypersaline relic seawater caught in sediments (Fig. 3). Brackish and salty groundwater from the inflow of estuarine seawater trapped in marshes has Cl/Br ratios around that of seawater (Table 2). The gradual contribution of unpolluted freshwater to the saline and hypersaline relic seawater is concentrated around a horizontal mixing line with varying Cl/Br ratios similar to seawater. Only one hypersaline sample representing evapoconcentrated relic seawater from the marsh has a Cl/Br ratio below 500 which may be explained by organic activity commonly affecting such saline water.

Curve IIIa is a horizontal evaporation line starting from present polluted rainwater, with average Cl/Br ratios around 500, producing phreatic water with similar Cl/Br ratios (Fig. 3). The use of this recent phreatic water for irrigation only produces evapoconcentration, which does not affect the original Cl/Br ratio of regional bulk deposition. It was sampled at the high/middle part of Rocina Creek, a representative groundwater drainage area with a short residence time, partly occupied by intensive agriculture. Curve IIIb is an upward convex mixing line of this evapoconcentrated phreatic water bearing agrochemicals derived from Br-based pesticides, as methyl-bromide, formerly used in sandy areas for soil fumigation in greenhouse strawberry production. Cl/Br ratios vary from 500, similar to average rainwater, to 350. A Br contribution is inferred up to 0.41 mg L^{-1} (Fig. 3). While baseline NO_3 concentration in natural areas is around 20 mg L^{-1} or less, NO_3 concentrations may be locally up to 200 mg L^{-1} due to the use of fertilizers (Manzano et al., 2001a).

Curve IV is an upward concave line of wastewater that includes dissolved NaCl in unpolluted old phreatic water (Fig. 3). The contribution of wastewater from domestic food preparation and cattle feeding increases the Cl/Br ratios up to 1000. This phreatic water, sampled in an open well at an isolated farm, shows Cl increases of up to 10.9 mg L^{-1} .

A local seawater sample taken from Torre de La Higuera Beach, in Matalascañas, shows slightly reduced salinity and a Cl/Br ratio of around 590. Although pollution by direct or indirect disposal of effluents or recent local groundwater discharge may cause some dilution, it should not significantly affect the marine Cl/Br ratio. This may therefore be due to either inaccurate analyses or to soil organic matter adsorption.

Wells, springs and galleries in the Canary Islands

The Canary Islands basically consists of deep submarine volcanic edifices piling up and followed by subaerial volcanics (mainly basaltic and acidic vulcanite differentiates), emitted in stages from 20 Ma to less than 1 Ma (million years), even historical eruptions. From the high central areas to the coast, the relief shows steep slopes that become gentle near the coast when not eroded, and it is generally abrupt with deep gullies. The climate varies from arid to semiarid with less than 100 mm year^{-1} rainfall at low altitudes near

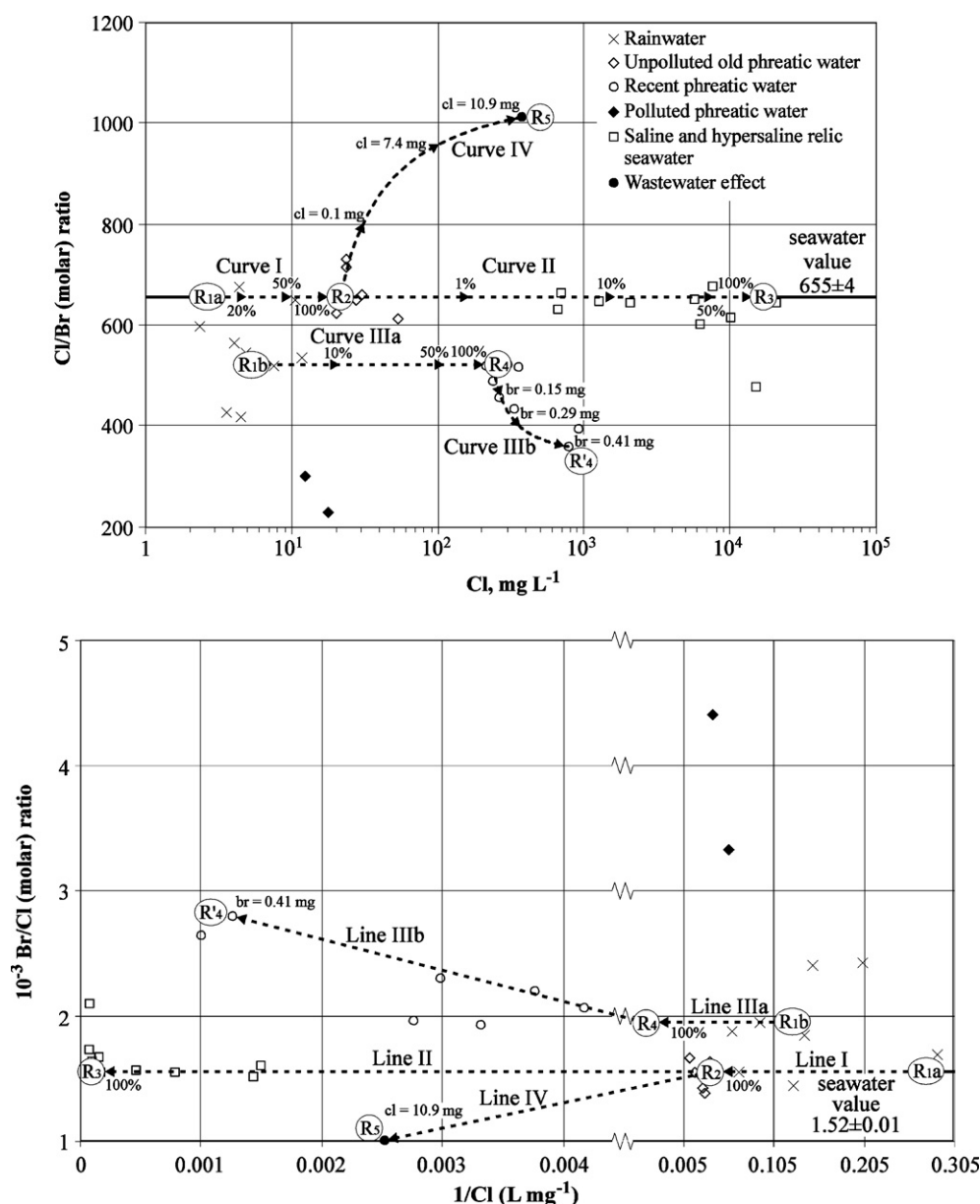


Figure 3 Plot of Cl/Br ratio vs. Cl (in mg L⁻¹) and plot of Br/Cl ratio vs. 1/Cl for samples from the Almonte-Marismas aquifer (Doñana). Circled numbers are distinctive end-members, R_{1a}: unpolluted rainwater; R_{1b}: polluted rainwater; R₂: unpolluted old phreatic water; R₃: saline and hypersaline relic seawater; R₄: recent phreatic water; R₄: water affected by agrochemicals; R₅: water affected by wastewater. Dissolution of a solid and/or mixing of end-members are shown by dotted lines; triangles indicate the proportion of mixing or solid solute added. Curve I: horizontal evapoconcentration line between R_{1a} and R₂ produced in recharge water. Curve II: R₂ mixing with R₃. Curve IIIa: horizontal evapoconcentration line between R_{1b} and R₄ produced in recharge water. Curve IIIb: incorporation of Br-based halides from agrochemicals to R₄. Curve IV: R₂ mixing with wastewater including dissolved NaCl.

the coast, to subhumid in the highlands (between 800 and 1500 m a.s.l.) with rainfall up to about 1000 mm year⁻¹, and again more arid conditions at the top of the higher islands (Gasparini et al., 1990; Cabrera and Custodio, 2004). Recharge is mainly from rainfall in the highlands and decreases (occasionally to less than 5 mm year⁻¹) in the lowlands near the coast (Custodio, 1992). Groundwater flows from the central high altitudes towards the deep gullies and the coast, where it discharges, mostly as diffuse flow. Intensive groundwater development has depleted the regional phreatic level, which is generally deep (Cabrera and Custodio, 2004). In the eastern islands, the lower elevations

produce a dominantly arid environment, with rainfall depths from 80 to 250 mm year⁻¹.

With the hydrogeological, geochemical and isotopic knowledge gained during the last decades (Custodio, 1988, 1990; Herrera and Custodio, 2003; Cabrera and Custodio, 2004), the main sources of natural salinity in most of the Canary Islands are now known, especially those related to the coastal saline recharge water affected by climatic aridity, and the local endogenous contribution of halides to groundwater, both affecting the low-salinity recharge at high altitudes (Gasparini et al., 1990; Custodio, 1988, 1990, 1992; Marrero et al., 2008). Localized marine

intrusion in some intensively developed coastal areas and several diffuse anthropogenic activities may contribute Cl to phreatic water, although background salinity is high due to the coastal arid climate (Custodio, 1988). These surveys have also provided information about some anthropogenic processes modifying natural salinity, especially intensive agriculture, which produces saline irrigation return flows. One hundred and five samples were taken of both natural and anthropogenic processes at selected points (wells, springs and galleries) in Tenerife, Gran Canaria, La Palma and Fuerteventura Islands (aquifer 24; Fig. 1), according to their well-known origin of salinity (unpublished data from S.N. Davis, A. Long and E. Custodio; Vegeer, 1991; Herrera and Custodio, 2003) (Table 2). All samples were plotted together and grouped by similar origin of salinity and sampling altitude into five groups (Fig. 4): (i) phreatic water in high and mid-slope areas, (ii) phreatic water in mid-slope areas affected by climatic evapoconcentration, (iii) phreatic water affected by coastal climatic aridity, (iv) endogenous contribution of halides and (v) agricultural pollution.

Accurate groundwater sampling provides Cl/Br ratio ranges for the main end-members mixed with unaffected phreatic water or added solutes. Three of these processes have been described in detail and plotted in Fig. 4.

Curve I in Fig. 4 is an upward concave mixing line of slightly saline phreatic water from the highlands with more saline phreatic water affected by the coastal arid climate at low altitude. Recharge water in the highlands has a Cl content between 4 and 20 mg L⁻¹ and Cl/Br ratios of around 500 or less. At lower altitudes, recharge water gradually becomes more saline, increasing the Cl content up to >1000 mg L⁻¹. Custodio and Herrera (2000) and Herrera and Custodio (2003) reported Cl/Br ratios up to 1000 and occasionally up to 2000 in bulk deposition (e.g., stations d33–d39; Fig. 1 and Table 1) and recent recharge water taken from low altitude springs and oozings in the southern windy coastal fringes of Fuerteventura Island, where climate condition is semiarid to arid (aquifer 22; Fig. 1 and Table 2) with persistent winds and rough seas and intense evapoconcentration. This results in a lower rainfall recharge rate and an atmospheric bulk Cl deposition rate of up to 10 g m⁻² year⁻¹ (stations d34 and d38; Table 1), which after evapoconcentration, makes phreatic water highly saline (Gasparini et al., 1990; Custodio, 1992). A relevant atmospheric dry deposition component contributing wind-blown halite from marine aerosols is an important fraction (up to 50%) of atmospheric bulk deposition. Different Curves I (Fig. 4) can be drawn depending on local hydrogeological and orographic features affecting Cl and Br in recharge water.

Curve II is an upward concave line of halides from local endogenous volcanic degassing into high and mid-slope phreatic water. The exsolved gases migrate towards the surface through fissures and high-permeability paths in the rock. When an aquifer is located between the magmatic environment and the surface, a fraction of the gases emitted are dissolved into the aquifer water. Springs affected systematically show Cl/Br ratios up to 1000, and higher Cl content than unaffected springs under the same hydrogeological conditions (Vegeer, 1991; Custodio and Herrera, 2000; Marrero et al., 2008). Depending on the relevance

of endogenous halides in groundwater, different Curves II can be drawn (Fig. 4).

Curve III is a smooth upward convex line resulting from a first horizontal evaporation line of water defined in Curve I (high-altitude phreatic water mixed with phreatic water affected by a coastal arid climate) plus an upward convex line of added solid solutes from Br-based agrochemicals used for soil fumigation in intensive agriculture. Water used to irrigate profitable large low-altitude agricultural plantations is partly supplied from natural springs, drainage galleries and deep-shaft wells, mainly in the highlands and at mid-slope, whether or not affected by climatic aridity. Catchment altitude controls the original salinity of phreatic water (several points on Curve I), while the agricultural use of water produces first evapoconcentration and then pollution; different Curves III can be drawn (Fig. 4). Cl/Br ratios oscillate from less than 250 to 350 depending on the relative contribution of Br-based agrochemicals to the phreatic water defining Curve I, which may be estimated at up to 0.07 mg L⁻¹ (Fig. 4). Up to 140 mg L⁻¹ in NO₃ and Cl/Br ratios between 220 and 380 are observed in phreatic water affected by agriculture, while the NO₃ content in unaffected phreatic water is less than 10 mg L⁻¹ for similar hydrogeological conditions (Herrera and Custodio, 2003; Cabrera and Custodio, 2004).

Discussion

The study of Cl/Br ratios in atmospheric bulk deposition has led to an understanding of the expectable chemical baseline of present groundwater in different places in Spain and Portugal. This source of knowledge allows natural and anthropogenic sources of pollution to be evaluated, and modern recharge by rainfall to be estimated using environmental chemical balances of atmospherically derived conservative substances (e.g., chloride ion), as well as estimating changes in groundwater along flow paths.

Orographic features and distance to the sea control the landward transport of Cl and Br ions from the ocean following the rain pathways, and gradually reduce the Cl/Br ratio. Rainfall coming from the northwest and southwest of the Iberian Peninsula produces Cl/Br ratios in bulk deposition similar to seawater or less in some cases, and Cl/Br ratios between 500 and 700 in unaffected coastal recharge water (Fig. 5 and Table 2). A similar pattern was reported in continental United States by Davis et al. (2004), though there it is more noticeable due to the much longer continental transport paths.

Superimposed on marine aerosols, other complementary natural and anthropogenic sources of Cl and Br are possible, mainly during prolonged summer and autumn dry periods, when relatively major airborne dust includes salinity from natural (mainly lithological) and anthropogenic sources (mainly urban and industrial). Dry deposition contributes Cl and Br fractions variable in space and time, depending on local lithology, anthropogenic activities and climate. The natural contribution of wind-blown halite from evaporitic rock outcrops including NaCl produces Cl/Br ratios of over 5000 during dry periods, while periods of continuous rainfall modulate average Cl/Br ratios down to 800 (e.g., stations d03, d12, d15, d17, d27; Fig. 1 and Table 1). The

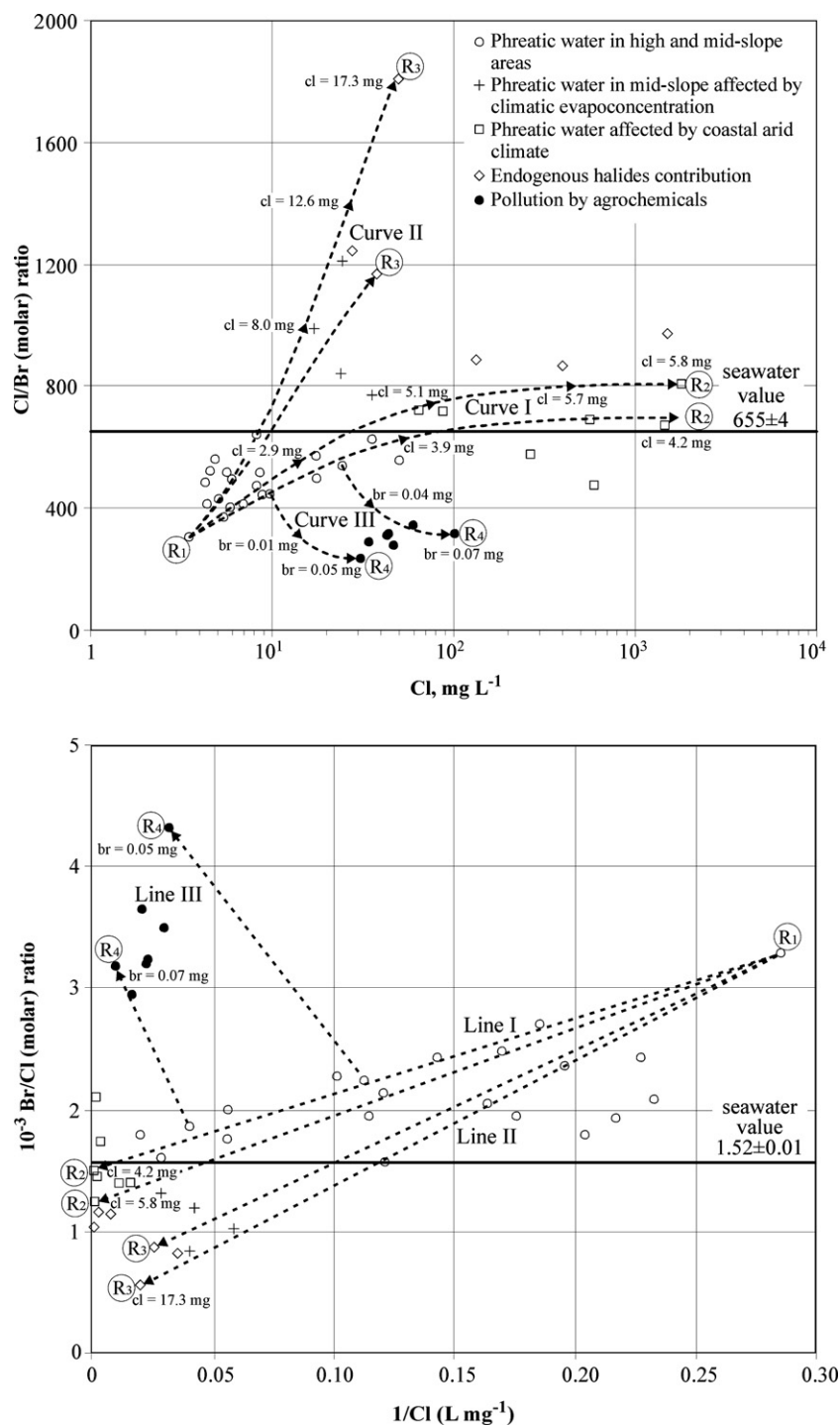


Figure 4 Plot of Cl/Br ratio vs. Cl (in mg L⁻¹) and plot of Br/Cl ratio vs. 1/Cl for wells, springs and galleries in Gran Canaria, Tenerife and La Palma (Canary Islands). Circled numbers are distinctive end-members, R_1 : high and mid-slope phreatic water; R_2 : phreatic water affected by coastal arid climate; R_3 : water affected by endogenous contribution of halides; R_4 : water affected by Br-based agrochemicals. Dissolution of a solid and/or mixing of end-members are shown by dotted lines; triangles indicate the proportion of mixing or solid solute added. Curve I: R_1 mixing with R_2 showing the gradual variation in the Cl/Br ratio in phreatic water from coastal arid zones with higher Cl/Br ratios towards the highlands where Cl/Br ratios are lower. Curve II: R_1 mixing with R_3 showing the gradual endogenous contribution of halides to phreatic water. Curve III: horizontal evapoconcentration line towards phreatic water defined in Curve II plus the gradual incorporation of Br-based halides from agrochemicals.

Cl/SO₄ ratio is clearly lower than seawater. This is the situation in major Spanish River basins and other minor basins, including Neogene gypsum formations.

The abundant anthropogenic contribution of particulate matter and halogens to the atmosphere from hydrocarbon and fuel combustion in urban and polluted industrial areas,

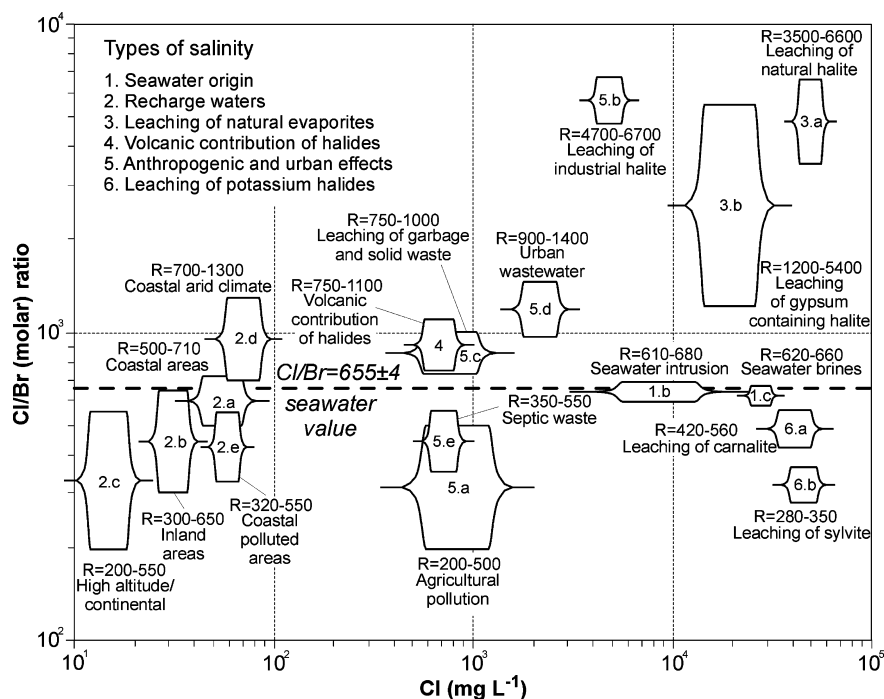


Figure 5 Plot of Cl/Br ratio vs. Cl (in mg L^{-1}) for six main salinity acquisition processes (including some subprocesses) described in 24 selected aquifers of Spain and Portugal, showing the Cl/Br ratio and Cl concentration ranges sampled; subprocess salinity codes are given in Table 2. Main types of salinity include: (i) seawater origin; (ii) different types of recharge water; (iii) water including leaching or dissolution of natural evaporites (halite and gypsum containing halite); (iv) water including volcanic halides; (v) water affected by anthropogenic salinity, including leaching of industrial and domestic halite; (vi) water and brine including leached potassium halides from salt mining areas.

and the use of Br-based agrochemicals in intensively irrigated areas produce Cl/Br ratios below that of seawater. Current recharge water in aquifers 04, 10, 12 and 20 (Fig. 1) shows this effect clearly, with Cl/Br ratios lower than the seawater ratio (Table 2). Following the western preferential rain and wind paths, the Cl/Br ratios are around 400 or less towards the east of Madrid (Fig. 1). Cl/Br ratios in bulk deposition vary between 400 and 550 in the polluted urban coastal areas of Barcelona and Aveiro (stations d05–d08 and d09–d11 Table 1), coinciding with the Cl/Br ratios found in recharge waters (Table 2). Prolonged dry periods without significant wind followed by short intense rainfall events produce Cl/Br ratios as low as 300 in Barcelona (station d05; Fig. 1), while dry deposition from marine aerosols shows a Cl/Br ratio up to 800 due to Cl removal in these coastal areas (Alcalá and Custodio, 2004). Martens et al. (1973) describe Cl/Br ratios between 480 and 600 in bulk deposition for similarly polluted urban coastal areas of Puerto Rico and San Francisco Bay, while Davis et al. (1998) describe Cl/Br ratios as low as 200 in other similarly polluted areas in the USA.

The southern coastal areas of some of the Canary Islands and the coastal fringe of the southeast Iberian Peninsula are semiarid to arid zones with rough seas, persistent winds and pronounced evaporation. High dry deposition yields average Cl/Br ratios greater than seawater and occasionally up to 2000 (e.g., stations d28, d32–d39; Fig. 1 and Table 1). Cl/SO₄ ratios and other ionic ratios in the bulk deposition are similar to seawater, thus discarding other lithological or anthropogenic salinity contributions. Nevertheless, follow-

ing the rain-cloud path, located at a higher altitude in these arid zones, Cl/Br ratios far from the coast are around the seawater ratio or lower. Cl/Br ratios in unaffected recharge water in these areas is in the same range, but differs locally where there is infiltration of surface runoff from higher altitudes (e.g., aquifers 13, 15, 21, 22, 23 and 24; Fig. 1).

Often, especially far from the coast, the Cl content and other substances incorporated by rainwater in recharge water cannot be explained by the marine aerosol chemical composition alone. In such cases, the atmospheric mineral deposition must be measured to model local hydrochemical behaviour based on mixtures of water from different hydrochemical origins.

Other non-atmospherically derived sources of salinity acting directly on the original groundwater salinity, such as dissolution of solids and water contributions from anthropogenic or natural sources (Custodio and Herrera, 2000; Alcalá and Custodio, 2005), limit the use of the groundwater chemical database available in Spain and Portugal for estimating recharge by rainfall through the chloride mass balance method. Since Cl and Br ions dissolved in groundwater maintain a reasonable record of the soluble matter composition (salts) generating its salinity, as well as the Cl/Br ratio, it is therefore possible to use the Cl/Br ratio to know the origin of local salinity from the regional spatial distribution of Cl/Br ratio in meteoric water.

Shallow groundwater sampled in coastal areas may be affected by seawater intrusion, added brine or evaporation of surface water, limiting its use for recharge estimation. In both cases, the original Cl/Br ratio is a poor tool for

clarifying the sources of salinity, except in arid coastal zones where the Cl/Br ratios are usually higher than seawater, allowing seawater intrusion and atmospheric saline contributions to be distinguished (Gasparini et al., 1990; Custodio, 1992). When salinity comes mostly from the marine aerosol, recharge water has Cl/Br ratios close to the seawater ratio of 655 ± 4 (Fig. 5), with a range of variation due mostly to variable dilution by freshwater, analytical uncertainty and some organic matter adsorption. Brackish groundwater from seawater sampled in Mediterranean and Atlantic coastal aquifers have similar Cl/Br ratios, which are somewhat lower than that of seawater ratio.

The original salinity of the water supply and added halite control the final Cl/Br ratio in natural water mixed with wastewater (Fig. 5). Average Cl added from halite may be up to 15 mg L^{-1} . Cl/Br ratios between 900 and 1400 were found for initial water supply with Cl/Br ratios between 300 and 800 (e.g., aquifers 1, 3, 4, 5, 6, 10, 11, 12, 16, 18 and 20; Fig. 1). Similar ranges and differences were reported by Vengosh and Pankratov (1998) and Davis et al. (1998, 2004) in urban wastewater from Israel and the USA. Sources of salinity leached from garbage and solid urban waste increase the Cl/Br ratios to between 750 and 1000 (Fig. 5). Industrial use of halite produces Cl/Br ratios between 4700 and 6700 (Fig. 5), similar in magnitude to natural halite leachates (Cl/Br ratios between 3500 and 6600, Fig. 5, and up to 40,000 if halite is the only source of solutes), which enables salinity from industrial waste and wastewater to be differentiated from halite leached from natural evaporitic formations. On the other hand, Cl/Br ratios of around 450 were reported in leachates derived from septic waste in Dehesas de Guadix (Moreno et al., 2000, aquifer 17; Fig. 1 and Table 2). Certain organic retention of Cl may be the cause, as proposed by Hudak (2003), for leachates from some farm-animal waste in Texas (USA). The Cl/Br ratio may be an additional tool for differentiating water effluents from domestic, farm and septic waste uses in joint urban wastewater management.

Br-based soil disinfectants were used for years as a pre-treatment for sandy soils to control nematodes in intensive greenhouse production of strawberries, tomatoes and other vegetables. Volatilised Br, which is carried by rainfall, may reduce Cl/Br ratios in phreatic water to between 200 and 500 (Fig. 5). Added Br from pesticides may be up to 0.5 mg L^{-1} . Cl/Br ratios below 300, and sometimes below 50 have been reported by Davis et al. (1998) in the USA. Low Cl/Br ratios are usually accompanied by high NO_3 content, which allows other sources of salinity to be differentiated.

The dissolution of sulphate-rich evaporites containing halite (NaCl) increases the Cl/Br ratios to between 1200 and 7500 in groundwater sampled in Spain (Fig. 5 and Table 2), though Cl/Br ratios up to 10,000 have been documented by McCaffrey et al. (1987) and Cartwright et al. (2004). When these geologic formations outcrop, the Cl/Br ratio may be up to 5000 in atmospheric bulk deposition during severe dry periods. Dry fallow fields may produce wind-blown halite-containing dust at basin scale and this may be a significant source of salinity in major inner river basins in Spain (Fig. 1), with similar Cl/Br ratios in recharge water. This is the case of aquifers 06, 07, 08, 10, 11, 17 and 18 (Fig. 1), and other similar large areas, limiting the use of groundwa-

ter samples for estimating recharge through the chloride mass balance method. A rise in Cl/Br ratios from recharge to discharge areas in detritic and/or carbonated aquifers 06, 08, 10, 11, 12 and 20 (Fig. 1), which include gypsum-rich layers containing halite, may be due to a gradual increase in water-rock interaction.

In the Llobregat River Basin potash mining area (aquifer 02; Fig. 1), several sodium and potassium halide and gypsum formations are now being worked (Ayora et al., 1995; ATLL, 2001; Soler et al., 2002). The original atmospherically dependent Cl/Br ratios of surface water in rivers and streams and groundwater has been progressively modified by the saline contribution from these mining operations. Effluent brines from potassium halide dissolution decrease the Cl/Br ratios to around 500 when carnalite is leached and around 300 for sylvite. Potash tailings in flotation dumps, consisting of several types of halides (carnalite, sylvite, halite, etc.), and other sulphate-rich evaporites (gypsum and anhydrite), produce Cl/Br ratios of around 500

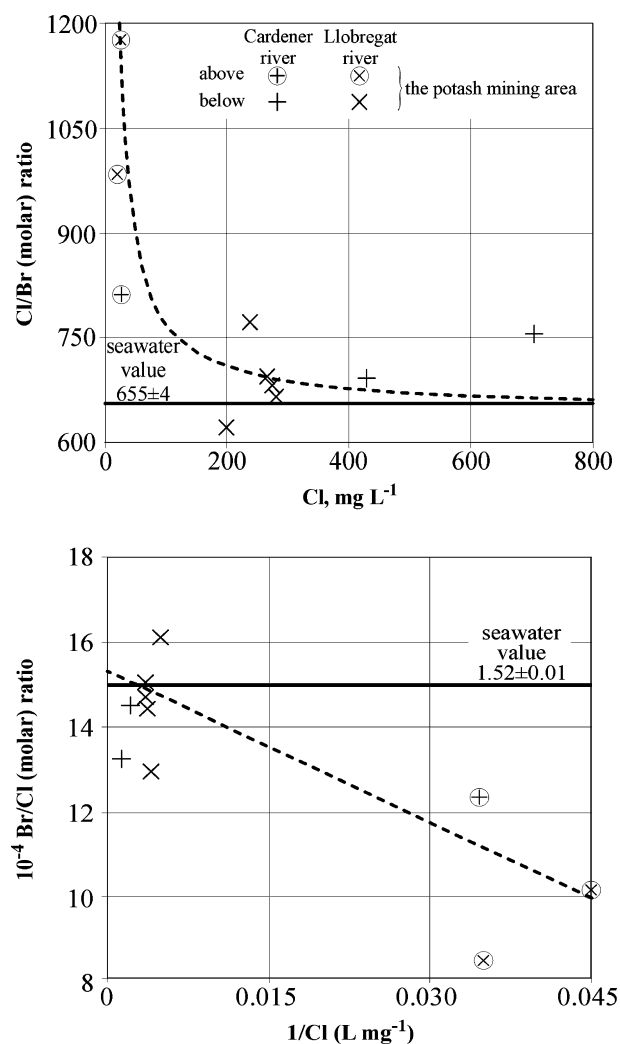


Figure 6 Plot of Cl/Br ratio vs. Cl (in mg L^{-1}) and plot of Br/Cl ratio vs. $1/\text{Cl}$ for the Llobregat and Cardener Rivers, above and below salt outcrops and potash mining areas. Values are medians for 1996–1999, after a brine collector was put into operation (data from ATLL, 2001).

(Fig. 5). Cl/Br ratios in oil-field brine (relics of evaporated seawater including precipitation of potassium halides) typically varied within the 100–300 range (Rittenhouse, 1967; Carpenter, 1978; Vengosh et al., 1998). An order of magnitude in Cl/Br ratios allows freshwater diluting pure halite, gypsum containing halite, carnalite, sylvite or other intermediate minerals to be distinguished. Median Cl/Br and Cl for the Llobregat River and its tributary, the Cardener (Fig. 1), with sampling stations up and downstream of the salt outcrops and potash mining are plotted in Fig. 6 (Martín-Alonso, 1994; ATLL, 2001). As Cl increases from saline contamination (mainly halite), the Cl/Br molar ratio tends to increase. Average Cl/Br ratios in the range of 600–750 means that the dominant source of pollution is not halite dissolution but mining effluents and tailing leachates, both related to K-rich minerals, also rich in Br. This direct information is very valuable for finding the end-members of mixed water in other similar Spanish Tertiary evaporitic basins, such as those in Navarra (Fig. 1).

In active volcanic areas, such as the Canary Islands, when an aquifer is located between the magmatic environment and the surface, a fraction of the gasses emitted are dissolved in the aquifer. The springs affected by endogenous degassing show Cl/Br ratios of up to 1000 (Vegeer, 1991; Custodio and Herrera, 2000). The exsolved CO₂ gas was used as a good tracer to identify high Cl/Br ratios due to the endogenous contribution of halides by wind-blown halite in coastal arid zones of the Canary Islands. Average Cl added from the endogenous contribution of halides may be up to 20 mg L⁻¹.

Conclusions

Orographic features and distance to the sea control the movement of Cl and Br ions inland from the ocean along rain pathways producing a progressive reduction in the Cl/Br ratio from around 655 to less than 300. Additional sources of Cl and Br are gradually added to the marine aerosol. Natural sources of Cl are mainly from halite, raising the Cl/Br ratios up to 1200 while anthropogenic sources mainly contribute Br-rich substances, lowering the Cl/Br ratios to 300. Cl/Br ratios in atmospheric bulk deposition control the ratios expectable in phreatic water affected only by saline evapo-concentration. Study of the Cl/Br ratio in bulk deposition allows groundwater with Cl derived from atmospheric sources to be distinguished from groundwater with Cl contributed by endogenous, lithological or anthropogenic sources. Several mixing processes and the addition of solid solutes affect the groundwater chemistry in many unconfined Spanish aquifers. Since they have different lithologies, groundwater flow systems, edaphic conditions and generally high water table, the mixtures may only be well-explained by studying the atmospheric bulk deposition.

Cl/Br ratios may increase up to 1500 in groundwater from the addition of halite in wastewater or leaching of solid waste and decrease to 300 from Br-based pesticides or farm-animal and septic waste. The endogenous contribution of halides in active volcanic areas of the Canary Islands, leaching and dissolution of natural and industrial halite, and the dissolution of sulphate-rich formations containing

halite may yield Cl/Br ratios between one thousand and several thousand.

When Cl content in groundwater is not affected by extreme evaporation, recharge by rainfall can be estimated by comparing Cl in atmospheric bulk deposition and unaffected shallow groundwater. In addition, complementary information on the groundwater flow paths may be supplied when Cl/Br ratios increase from continuous contribution of Cl from lithology.

Experience gained in Spain and Portugal is a source of knowledge to use the Cl/Br ratio as an effective tracer in other mid-latitudes Mediterranean countries (southern Europe and northern Africa) with similar orographic, geological and climatic conditions.

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Appendix A. Mixing and addition of solid solutes modifying the original Cl/Br ratio

A given water composition may be changed by mixing with other water or by dissolving a solid, which modifies the original Cl and Br concentration, and consequently the Cl/Br molar ratio. If: (i) I, F and A are the initial, final (mixed) and added water, respectively; (ii) S is the dissolved solid per unit water volume; (iii) Cl, Br and R represent chloride, bromide and the Cl/Br molar ratio in I, F and A (sub-index); (iv) Cl and Br are the Cl and Br fractions in the solid, where $r = \text{Cl}/\text{Br}$; (v) $X = \text{fraction of I}$ and $1 - X = \text{fraction of A}$ in the final (mixed) solution, all of them in the same units (here molar quantities); the mass conservation balance yields:

(a) Admixture of a fraction X of water A to water I (Fig. 2a):

$$R_F = \frac{\text{Cl}_F}{\text{Br}_F} = \frac{\text{Cl}_I}{\text{Br}_I(1 - X) + \text{Br}_A \cdot X} \quad (1)$$

Since $\text{Cl}_F = \text{Cl}_I(1 - X) + \text{Cl}_A \cdot X$; where $X = \frac{\text{Cl}_F - \text{Cl}_I}{\text{Cl}_A - \text{Cl}_I}$.

Then, after substituting X and rearranging the result, and taking into account that $Cl_i/Br_i = R_i$ and $Cl_A/Br_A = R_A$:

$$R_F = Cl_F \frac{Cl_A - Cl_i}{\left(\frac{Cl_i}{R_i} - \frac{Cl_A}{R_A}\right)(Cl_A - Cl_F)} \quad (2)$$

In a plot of R vs. Cl (the actual R_F and Cl_F) the admixture of a fraction X of water A follows a curve with an unchanging slope sign (Fig. 2a). By taking decimal logarithms Eq. (2) becomes:

$$\log R_F = \log Cl_F - \log(Cl_A - Cl_F) + \log \frac{Cl_A - Cl_i}{\frac{Cl_i}{R_i} - \frac{Cl_A}{R_A}} \quad (3)$$

Only when $\log(Cl_A - Cl_F)$ is small, the $\log R$ vs. $\log Cl$ plot is a 45° diagonal displaced by the third term. This is frequently done in the literature to cover the wide range of Cl , but there is deviation from the straight line.

In a plot of $1/R$ vs. $1/Cl$ the admixture follows a straight line with slope M and intercept N , connecting points I and A (Fig. 2a):

$$\frac{1}{R_F} = \frac{\frac{Cl_A}{R_A} - \frac{Cl_i}{R_i}}{Cl_A - Cl_i} + \frac{Cl_A \left(\frac{Cl_i}{R_i} - \frac{Cl_A}{R_A}\right)}{Cl_A - Cl_i} \frac{1}{Cl_F} = N + M \frac{1}{Cl_F} \quad (4)$$

where $N \equiv \frac{\frac{Cl_A}{R_A} - \frac{Cl_i}{R_i}}{Cl_A - Cl_i}$ and $M \equiv \frac{Cl_A \left(\frac{Cl_i}{R_i} - \frac{Cl_A}{R_A}\right)}{Cl_A - Cl_i}$

(b) Dissolution of a solid (Fig. 2b):

$$R_F = \frac{Cl_F}{Br_F} = \frac{Cl_F}{Br_i + S \cdot br} \quad (5)$$

assuming there is no significant change in volume (for low salinity).

Since $Cl_F = Cl_i + S \cdot cl$; where $S = \frac{Cl_F - Cl_i}{cl}$.

Substituting S and rearranging the result:

$$R_F = \frac{Cl_F R_i r}{Cl_i(r - R_i) + R_i Cl_F} \quad (6)$$

In a plot of R vs. Cl the gradual addition of the solute follows a curve with an unchanging slope sign (Fig. 2b). By taking decimal logarithms, Eq. (6) becomes:

$$\log R_F = \log Cl_F - \log [Cl_i(r - R_i) + R_i Cl_F] + \log R_i r \quad (7)$$

Only when $\log [Cl_i(r - R_i) + R_i Cl_F]$ is small the plot of $\log R$ vs. $\log Cl$ is a 45° diagonal displaced by the third term.

In a plot of $1/R$ vs. $1/Cl$ this addition may be interpreted by means of a linear relationship (Fig. 2b):

$$\frac{1}{R_F} = \frac{1}{r} + Cl_i \left(\frac{1}{R_i} - \frac{1}{r} \right) \frac{1}{Cl_F} \quad (8)$$

with a slope $Cl_i \left(\frac{1}{R_i} - \frac{1}{r} \right)$ and intercept $1/r$.

References

- Aiuppa, A., Federico, C., Franco, A., Giudice, G., Gurrieri, S., Inguaggiato, S., Liuzzo, M., McGonigle, A.J.S., Valenza, M., 2005. Emission of bromine and iodine from Mount Etna volcano. *Geochemistry, Geophysics and Geosystems* 6, Q08008. doi: 10.1029/2005GC000965.
- Alcalá, F.J., 2006. Recarga a los acuíferos españoles mediante balance hidrogeológico. Ph.D. Thesis, Universitat Politècnica de Catalunya, Barcelona, 719 pp. (in Spanish with abstract in English).
- Alcalá, F.J., Custodio, E., 2004. Deposition total atmosférica de elementos mayoritarios en la ciudad de Barcelona (NE de España). Datos preliminares sobre la aportación mineral por la precipitación atmosférica. In: IAH-Spanish Group (Eds.), *Simpósio Sobre el Agua y la Ciudad Sostenible: Hidrogeología Urbana*. IGME, Barcelona, pp. 277–287.
- Alcalá, F.J., Custodio, E., 2005. Use of the Cl/Br ratio as a tracer to identify the origin of salinity in some coastal aquifers of Spain. In: Araguás, L., Custodio, E., Manzano, M. (Eds.), *Proceedings of the 18th Salt Water Intrusion Meeting*. IGME, Cartagena, pp. 481–497.
- Alcalá, F.J., Custodio, E., 2007. Recharge by rainfall to Spanish aquifers through chloride mass balance in the soil. In: Ribeiro, L., Chambel, A., Condeso de Melo, M.T. (Eds.), *Proceedings of the XXXV IAH Congress: Groundwater and Ecosystems*, Lisboa, 10 pp. (abstract book: paper 236).
- Alcalá, F.J., Custodio, E., 2008. Atmospheric chloride deposition in continental Spain. *Hydrological Processes* 22. doi:10.1002/hyp.6965.
- ATLL, 2001. Variacions espacials i temporals en la qualitat de l'aigua de la conca del riu Llobregat: parametres inorgànics, 1996–1999. *Recull 5* (Feb. 2001), *Quaderns ATLL* (Aigües Ter-Llobregat), Barcelona, 122 pp.
- Ayora, C., Taberner, C., Pierre, C., Pueyo, J.J., 1995. Modeling the sulfur and oxygen isotopic composition of sulfates through a halite-potash sequence: implications for the hydrological evolution of the Upper Eocene South Pyrenean basin. *Geochimica et Cosmochimica Acta* 59 (9), 1799–1808.
- Bayó, A., Custodio, E., Loaso, C., 1997. Las aguas subterráneas en el delta del Ebro. *Revista de Obras Públicas* 144 (3368), 47–65.
- Bello, A., López-Pérez, J.A., Díaz-Viruliche, L., Tello, J., 2001. Alternatives to methyl bromide for soil fumigation in Spain. In: Labrada, R., Fornasari, L. (Eds.), *Global Report on Validated Alternatives to the Use of Methyl Bromide for Soil Fumigation*, 336. FAO, Roma, pp. 33–46.
- Bobrowski, N., Hönninger, G., Galle, B., Platt, U., 2003. Detection of bromine monoxide in a volcanic plume. *Nature* 423, 273–276.
- Bureau, H.E., Métrich, N., 2003. An experimental study of bromine behaviour in water-saturated silicic melts. *Geochimica et Cosmochimica Acta* 67 (9), 1689–1697.
- Butler, J.H., King, D.B., Lobert, J.M., Montzka, S.A., Yvon-Lewis, S.A., Hall, B.D., Warwick, N.J., Mondeel, D.J., Aydin, M., Elkins, J.W., 2007. Oceanic distributions and emissions of short-lived halocarbons. *Global Biogeochemistry Cycles* 21, GB1023. doi: 10.1029/2006GB002732.
- Cabrera, M.C., Custodio, E., 2004. Groundwater flow in a volcanic-sedimentary coastal aquifer: Telde area, Gran Canaria, Canary Islands, Spain. *Hydrogeology Journal* 12 (3), 305–320.
- Cabrera, M.C., Delgado, F., Muñoz, J., Pérez Torrado, F.J., La Moneda, E., 2000. Caracterización de las familias hidrogeológicas en el acuífero de La Aldea (Gran Canaria). *Geotemas* 1 (2), 47–50.
- Carpenter, A.B., 1978. Origin and chemical evolution of brines in sedimentary basins. *Circular 79*, Oklahoma Geological Survey, pp. 60–77.
- Cartwright, I., Weaver, T.R., Fulton, S., Nichol, C., Reid, M., Cheng, X., 2004. Hydrogeochemical and isotopic constraints on the origins of dryland salinity, Murray Basin, Victoria, Australia. *Applied Geochemistry* 19, 1233–1254.
- Cartwright, I., Weaver, T.R., Fifield, L.K., 2006. Cl/Br ratios and environmental isotopes as indicators of recharge variability and groundwater flow: an example from the southeast Murray Basin, Australia. *Chemical Geology* 231, 38–56.
- Castañeda, C., García-Vera, M.A., 2008. Water balance in the playalakes of an arid environment, Monegros, NE Spain. *Hydrogeology Journal* 16 (1), 87–102.

- Ceballos-Barbancho, A., Morán-Tejeda, E., Luengo-Ugidos, M.A., Llorente-Pinto, J.M., 2008. Water resources and environmental change in a Mediterranean environment: the south-west sector of the Duero river basin (Spain). *Journal of Hydrology* 351 (1–2), 126–138.
- Cicerone, R.J., 1981. Halogens in the atmosphere. *Review of Geophysics and Space Physics* 19 (1), 123–139.
- Condeso de Melo, M.T., Carreira Paquete, P.M.M., Marques da Silva, M.A., 2001. Evolution of the Aveiro Cretaceous aquifer (NW Portugal) during the Late Pleistocene and present day: evidence chemical and isotopic data. In: Edmunds, W.M., Milne, C. (Eds.), *Paleowaters in Coastal Europe: Evolution of Groundwater since the Late Pleistocene*. Special Publications 189. Geological Society, London, pp. 139–154.
- Contreras, S., Boer, M., Alcalá, F.J., Domingo, F., García, M., Pulido-Bosch, A., Puigdefábregas, J., 2008. An ecohydrological modelling approach for assessing long-term recharge rates in semiarid karstic landscapes. *Journal of Hydrology* 351 (1–2), 42–57.
- Custodio, E., 1988. Nota sobre la intrusión marina en las Islas Canarias. In: Fernández-Rubio, R., López Geta, J.A., Ramos, G. (Eds.), *Tecnología de la Intrusión Marina en Acuíferos Costeros*, vol. 1. IGME, Madrid, pp. 593–603.
- Custodio, E., 1990. Saline groundwater in the Canary Islands (Spain) resulting from aridity. *Greenhouse Effect, Sea Level and Drought* NATO ASI Series C: Mathematical and Physical Sciences, vol. 325. Kluwer, Dordrecht, pp. 593–618.
- Custodio, E., 1992. Coastal aquifer salinization as a consequence of aridity: the case of Amurga phonolitic massif, Gran Canaria Island. In: Custodio, E., Galofré, A. (Eds.), *Proceedings of the 12th Study and Modelling of Saltwater Intrusion*. CIMNE-UPC, Barcelona, pp. 81–98.
- Custodio, E., 1994. Endurecimiento del agua del Valle Bajo del Llobregat por cambios en los procesos de recarga. In: IAH-Spanish Group (Ed.), *Análisis y Evolución de la Contaminación de las Aguas Subterráneas*, vol. 2. IAH, Alcalá de Henares, pp. 123–140.
- Custodio, E., 1997. Evaluación de la recarga por la lluvia mediante métodos ambientales químicos, isotópicos y térmicos. In: Custodio, E., Llamas, M.R., Samper, J. (Eds.), *La Evaluación de la Recarga a los Acuíferos en la Planificación Hidrológica*. IGME and IAH-Spanish Group, Las Palmas de Gran Canaria, Madrid, pp. 83–110.
- Custodio, E., 2000. Groundwater-dependent wetlands. *Acta Geologica Hungarica* 43 (2), 173–202.
- Custodio, E., Llamas, M.R., 1983. *Hidrología Subterránea*. Omega, Barcelona, 2350 pp.
- Custodio, E., Palancar, M., 1995. Las aguas subterráneas en Doñana. *Revista de Obras Públicas* 142 (3340), 31–53.
- Custodio, E., Herrera, C., 2000. Utilización de la relación Cl/Br como trazador hidrogeoquímico en hidrología subterránea. *Boletín Geológico y Minero* 111 (4), 49–67.
- Custodio, E., Alcalá, F.J., 2004. Modificación del cociente Cl/Br y otras relaciones iónicas en el proceso de tratamiento de aguas subterráneas por ósmosis inversa. *Hidrogeología y Recursos Hidráulicos* 26, 325–335.
- Custodio, E., Edmunds, W.M., Travi, Y., 2001. Management of coastal palaeowaters. In: Edmunds, W.M., Milne, C. (Eds.), *Paleowaters in Coastal Europe: Evolution of Groundwater since the Late Pleistocene*. Special Publications 189. Geological Society, London, pp. 313–327.
- Delmelle, P., Bernard, A., 1994. Geochemistry, mineralogy, and chemical modelling of the acid water lake of Kawah Ijen volcano, Indonesia. *Geochimica et Cosmochimica Acta* 58 (11), 2445–2460.
- Davis, S.N., Whittemore, D.O., Fabryka-Martin, J., 1998. Uses of chloride/bromide ratios in studies of potable water. *Ground Water* 36 (2), 338–350.
- Davis, S.N., Fabryka-Martin, J., Wolfsberg, L.E., 2004. Variations of bromide in potable ground water in the United States. *Ground Water* 42 (6), 902–909.
- De Cal, A., Martínez-Trecheño, A., Salto, T., López-Aranda, J.M., Melgarejo, P., 2005. Effect of chemical fumigation on soil fungal communities in Spanish strawberry nurseries. *Applied Soil Ecology* 28 (1), 47–56.
- Dror, G., Ronen, D., Stiller, M., Nishri, A., 1999. Cl/Br ratios of Lake Kinneret, pore water and associated springs. *Journal of Hydrology* 225 (3), 130–139.
- Duce, R., Winchester, J.W., Van Nahl, T.W., 1965. Iodine, bromide and chloride in the Hawaiian marine atmosphere. *Journal of Geophysical Research* 70, 1775–1779.
- Eastoe, Ch.J., Long, A., Knauth, L.P., 1999. Stable chlorine isotopes in the Palo Duro Basin, Texas: evidence for preservation of Persian evaporate brines – I. Theory. *Geochimica et Cosmochimica Acta* 63 (9), 1375–1382.
- Edmunds, W.M., 2001. Palaeowaters in European coastal aquifers – the goals and main conclusions of the PALAEWAUX project. In: Edmunds, W.M., Milne, C. (Eds.), *Paleowaters in Coastal Europe: Evolution of Groundwater since the Late Pleistocene*. Special Publications 189. Geological Society, London, pp. 1–16.
- Eriksson, E., 1960. The yearly circulation of chloride and sulphur in nature; meteorological, geochemical and pedological implications. Part II. *Tellus* 12, 63–109.
- Fabryka-Martin, J., Whittemore, D.O., Davis, S.N., Kubik, P.W., Sharma, P., 1991. Geochemistry of halogens in the Milk River aquifer, Alberta, Canada. *Applied Geochemistry* 6, 447–464.
- Falgàs, E., Ledo, J., Teixidó, T., Gabàs, A., Ribera, F., Arango, C., Queralt, P., Plata, J.L., Rubio, F.M., Peña, J.A., Martí, A., Marcuello, A., 2005. Geophysical characterization of a mediterranean coastal aquifer: the baixa Tordera fluvio-deltaic aquifer unit (Barcelona, NE Spain). In: Araguás, L., Custodio, E., Manzano, M. (Eds.), *Proceedings of the 18th Salt Water Intrusion Meeting*. IGME, Cartagena, pp. 395–404.
- Fernández-Uría, A., Fontes, J.Ch., Herráez, J., Llamas, M.R., Luisa-Rubio, P.L., 1985. Tridimensional groundwater chemical and isotopic variations as related to the Madrid aquifer flow system. *Estudios Geológicos* 41, 229–236.
- Fontes, J.Ch., Matray, J.M., 1993. Geochemistry and origin of formation brines from the Paris Basin, France: 2. Saline solutions associated with oil fields. *Chemical Geology* 109, 177–200.
- Fontes, J.Ch., Yousefi, M., Allison, G.B., 1986. Estimation of the long-term groundwater discharge in the Northern Sahara using stable isotope profiles in soil water. *Journal of Hydrology* 86, 315–327.
- Freeman, J.T., 2007. The use of bromide and chloride mass ratios to differentiate salt-dissolution and formation brines in shallow groundwater of the Western Canadian Sedimentary Basin. *Hydrogeology Journal* 15 (7), 1377–1385.
- Fruchter, J.S., Robertson, D.E., Evans, J.C., Olsen, K.B., Lepel, E.A., Laul, J.C., Abel, K.H., Sanders, R.W., Jackson, P.O., Wogman, N.S., Perkins, R.W., Van Tuyl, H.H., Beauchamp, R.H., Shade, J.W., Daniel, J.L., Erikson, R.L., Sehmel, G.A., Lee, R.N., Robinson, A.V., Moss, O.R., Briant, J.K., Cannon, W.C., 1980. Mount St. Helens ash from the 18 May 1980 eruption: chemical, physical, mineralogical and biological properties. *Science* 209 (4461), 1116–1125.
- Gasparini, A., Custodio, E., Fontes, J.Ch., Jiménez, J., Núñez, J.A., 1990. Exemple d'étude géochimique et isotopique de circulations aquifères en terrain volcanique sous climat semi-aride (Amurga, Gran Canaria, Illes Canaries). *Journal of Hydrology* 114, 61–91.
- Gerritse, R.G., George, R.J., 1988. The role of soil organic matter in the geochemical cycling of chloride and bromide. *Journal of Hydrology* 101 (1–4), 83–95.
- Giménez, E., Morell, I., 1997. Hydrogeochemical analysis of salinization processes in the coastal aquifer of Oropesa (Castellón, Spain). *Environmental Geology* 29 (1–2), 118–131.

- Gisbert, J., Pulido-Bosch, A., Al Alwani, G., 1998. On the characterization of hydrologic behavior of a high mountain schistous catchment. *Münchener Geologische Hefte* B8, 29–34.
- Goni, I.B., Fellman, E., Edmunds, W.M., 2001. Rainfall geochemistry in the Sachel region of northern Nigeria. *Atmospheric Environment* 35 (25), 4331–4339.
- Hautman, D.P., Munch, D.J., 1997. EPA 300 1. Determination of Inorganic Anions in Drinking Water by Ion Chromatography. Revision 1.0. USEPA, Office of Water. EPA, Cincinnati, OH, 40 pp.
- Herczeg, A.L., Dogramaci, S.S., Leaney, F.W., 2001. Origin of dissolved salts in a large, semi-arid groundwater system: Murray Basin, Australia. *Marine and Freshwater Resources* 52, 41–52.
- Herrera, C., Custodio, E., 2003. Hipótesis sobre el origen de la salinidad de las aguas subterráneas en la isla de Fuerteventura, Archipiélago de Canarias, España. *Boletín Geológico y Minero* 114 (4), 433–452.
- Herrmann, A.G., 1972. Bromine distribution coefficients for halite precipitated from modern sea water under natural conditions. *Contributions to Mineralogy and Petrology* 37 (3), 249–252.
- Hudak, P.F., 2003. Chloride/bromide ratios in leachate derived from farm-animal waste. *Environmental Pollution* 121, 23–25.
- Iribar, V., Carrera, J., Custodio, E., Medina, A., 1997. Inverse modelling of seawater intrusion in the Llobregat delta deep aquifer. *Journal of Hydrology* 198 (1–4), 226–247.
- ITGE, 1992. Hidrogeología del Parque Nacional de Doñana y su entorno. Colección Informes Aguas Subterráneas y Geotecnia. Geological Survey of Spain, Internal Report, Madrid, 64 pp. (in Spanish).
- ITGE, 1994. Las aguas subterráneas del Campo de Cartagena (Murcia). Geological Survey of Spain, Internal Report, Madrid (in Spanish).
- ITGE-DGOHCA, 1999. Programa de actualización del inventario hidrogeológico (PAIH). Análisis del conocimiento actual. Evaluación y programación de estudios en las cuencas intercomunitarias. Geological Survey of Spain, Internal Report, Madrid (in Spanish).
- Kloppmann, W., Negrel, Ph., Casanova, J., Klinge, H., Schelkes, K., Guerrot, C., 2001. Halite dissolution derived brines in the vicinity of a Permian salt dome (N German Basin). Evidence from boron, strontium, oxygen, and hydrogen isotopes. *Geochimica et Cosmochimica Acta* 65 (22), 4087–4101.
- Koglin, E.N., 1984. Bromide as an environmental tracer in groundwater of Tucson Basin, Arizona. M.S. Thesis, Department of Hydrology and Water Resources, University of Arizona, Tucson.
- Kohfahl, C., Rodríguez, M., Fenk, C., Menz, C., Benavente, J., Hubberten, H., Meyer, H., Paul, L., Knappe, A., López-Geta, J.A., Pekdeger, A., 2008. Characterising flow regime and interrelation between surface-water and ground-water in the Fuente de Piedra salt lake basin by means of stable isotopes, hydrogeochemical and hydraulic data. *Journal of Hydrology* 351 (1–2), 170–187.
- Kolodny, Y., Katz, A., Starinsky, A., Moise, T., Simon, E., 1999. Chemical tracing of salinity sources in Lake Kinneret (Sea of Galilee), Israel. *Limnology and Oceanography* 44 (4), 1035–1044.
- Lehmann, B.E., Davis, S.N., Fabryka-Martin, J.T., 1993. Atmospheric and subsurface sources of stable and radioactive nuclides used for groundwater dating. *Water Resources Research* 29, 2027–2040.
- López, J.M., Mateos, R.M., 2003. La intrusión marina en los acuíferos de la isla de Mallorca. In: López-Geta, J.A., de la Orden, J.A., Gómez, J.D., Ramos, G., Mejías, M., Rodríguez, L. (Eds.), *Tecnología de la Intrusión de Agua de Mar en Acuíferos Costeros: Países Mediterráneos*, vol. 1. IGME, Madrid, pp. 383–392.
- Manzano, M., Custodio, E., Loosli, H.H., Cabrera, M.C., Riera, X., Custodio, J., 2001a. Palaeowater in coastal aquifers of Spain. In: Edmunds, W.M., Milne, C. (Eds.), *Paleowaters in Coastal Europe: Evolution of Groundwater since the Late Pleistocene*. Special Publications 189. Geological Society, London, pp. 107–138.
- Manzano, M., Soler, A., Carrera, J., Custodio, J., 2001b. Composición isotópica (^{18}O , ^2H , ^{34}S) de las aguas del área afectada por el vertido minero de Aznalcóllar (SO España). In: Medina, A., Carrera, J., Vives, L. (Eds.), *Las Caras del Agua Subterránea*. Serie Hidrogeología y Aguas Subterráneas, vol. 1. IGME, Madrid, pp. 477–487.
- Marrero, R., López, D.L., Hernández, P.A., Pérez, N.M., 2008. Carbon dioxide discharged through the Las Cañadas Aquifer, Tenerife, Canary Islands. *Pure and Applied Geophysics*. doi: 10.1007/s00024-007-0287-3.
- Martens, C.S., Wesolonsky, J.J., Harns, R.C., Kaifer, R., 1973. Chloride loss from Puerto Rico and San Francisco Bay area marine aerosols. *Journal of Geophysical Research* 82, 8778–8791.
- Martin-Alonso, J., 1994. Barcelona's water supply improvement: the brine collector of the Llobregat river. *Water Science and Technology* 30 (10), 221–227.
- McCaffrey, M.A., Lazar, B., Holland, H.D., 1987. The evaporation path of seawater and the coprecipitation of Br^- and K^+ with halite. *Journal of Sedimentary Petrology* 57, 928–937.
- MIMAM, 2000. The white book of the water in Spain. Ministry of the Environment, Secretary of Waters and Coast, General Direction of Hydraulic Works and Water Quality, Madrid, 637 pp. (in Spanish).
- Minor, T.B., Russell, C.E., Mizell, S.A., 2007. Development of a GIS-based model for extrapolating mesoscale groundwater recharge estimates using integrated geospatial data sets. *Hydrogeology Journal* 15, 183–195.
- Montes, J., Vázquez-Suñé, E., 2005. Hidrogeología de Badalona. Ajuntament de Badalona, 83 pp. (in Spanish).
- Moreno, L., Lliquiñano, M.C., Rubio, J.C., Murillo, J.M., 2000. Eliminación de aguas residuales urbanas mediante filtración directa sobre el terreno. Impacto sobre el sistema solución del suelo-agua subterránea. *Boletín Geológico y Minero* 111 (5), 47–62.
- Öberg, G., Sandén, P., 2005. Retention of chloride in soil. *Hydrological Processes* 19, 2123–2136.
- Panno, S.V., Hackley, K.C., Hwang, H.H., Greenberg, S.E., Krapac, I.G., Landsberger, S., O'Kelly, D.J., 2006. Characterization and identification of Na-Cl sources in groundwater. *Ground Water* 44 (2), 176–187.
- Park, J., Bethke, C.M., Torgersen, T., Johnson, T.M., 2002. Transport modeling applied to the interpretation of groundwater ^{36}Cl age. *Water Resources Research* 38 (5), 1–15.
- Pascual, M., Bayó, A., 1991. La sobreexplotación del acuífero de Vicfred-Guisona (Lérida). Posibilidades de recuperación con aguas superficiales del Canal de Urgell. In: AIH-Spanish Group (Eds.), *Sobreexplotación de Acuíferos*. Puerto de la Cruz (Tenerife), pp. 235–239.
- Querol, X., Alastuey, A., De la Rosa, J., Plana, F., Ruiz, C.R., 2002. Source apportionment analysis of atmospheric particulates in an industrialised urban site (Huelva City) in South-western Spain. *Atmospheric Environment* 36 (19), 3113–3125.
- Redeker, K.R., Wang, N.Y., Low, J.C., McMillan, A., Tyler, S.C., Cicerone, R.J., 2000. Emissions of methyl halides and methane from rice paddies. *Science* 290 (5493), 966–969.
- Risacher, F., Fritz, B., Alonso, H., 2006. Non-conservative behaviour of bromine in surface waters and brines of Central Andes: a release into the atmosphere? *Geochimica et Cosmochimica Acta* 70 (9–1), 2143–2152.
- Rittenhouse, G., 1967. Bromide in oil field waters and its use in determining possibilities of origin of these waters. *American Association Petroleum Geology Bulletin* 51 (12), 2430–2440.

- Rosenthal, E., 1987. Chemical composition of rainfall and ground-water in recharge areas of the Bet Shean-Harod multiple aquifer system, Israel. *Journal of Hydrology* 89 (3–4), 329–352.
- Salvany, J.M., Custodio, E., 1995. Características litoestratigráficas de los depósitos plio-cuaternarios del Bajo Guadalquivir en el área de Doñana: implicaciones hidrogeológicas. *Revista de la Sociedad Geológica de España* 8 (1–2), 21–31.
- Sanchez-Martos, F., Pulido-Bosch, A., Molina, L., Vallejos, Á., 2002. Identification of the origin of salinization in groundwater using minor ions (Lower Andarax, Southeast Spain). *The Science of the Total Environment* 297 (1), 43–58.
- Schaefer, L., Fegley, B., 2005. Alkali and halogen chemistry in volcanic gases on Io. *Icarus* 173 (2), 454–468.
- Soler, A., Canals, A., Goldstein, S.L., Otero, N., Antich, N., Spangenberg, J., 2002. Sulfur and strontium isotope composition of Llobregat River (NE Spain): tracers of natural and anthropogenic chemicals in stream waters. *Water, Air, and Soil Pollution* 136, 207–224.
- Solomon, S., Thompson, D.W.J., Portmann, R.W., Oltmans, S.J., Thompson, A.M., 2005. On the distribution and variability of ozone in the tropical upper troposphere: implications for tropical deep convection and chemical–dynamical coupling. *Geophysical Research Letters* 32, L23813. doi:10.1029/2005GL024323.
- Stevens, C.R., 1990. Variations of Cl/Br ratios in ground water of Tucson Basin and Avra Valley, Arizona. M.S. Report, Department of Geosciences, University of Arizona, Tucson.
- Suso, J., Llamas, M.R., 1993. Influence of groundwater development of the Doñana National Park ecosystems (Spain). *Journal of Hydrology* 141 (1–4), 239–270.
- Taberner, C., Cendón, D.I., Pueyo, J.J., Ayora, C., 2000. The use of environmental markers to distinguish marine vs. continental deposition and to quantify the significance of recycling in evaporite basins. *Sedimentary Geology* 127 (3–4), 213–240.
- Vázquez, I., de la Fuente, P., 2007. Exactitud y precisión de la cromatografía iónica de alta resolución (HPIC) en el estudio hidrogeológico de aniones y relaciones iónicas. In: Pulido-Bosch, A., IIIII, López-Geta, J.A., Ramos, G. (Eds.), *Simposio Internacional sobre Tecnología de la Intrusión de Agua de Mar en Acuíferos Costeros*, 1. IGME, Madrid, pp. 831–838.
- Vegeer, A.I., 1991. Geochemical methods for evaluating the origin and evolution of groundwater in volcanic rocks. Ph.D. Thesis, Department of Hydrology and Water Resources, University of Arizona, Tucson, 251 pp.
- Vengosh, A., Pankratov, I., 1998. Chloride/bromide and chloride/fluoride ratios of domestic sewage effluents and associated contaminated groundwater. *Ground Water* 36 (5), 815–824.
- Vengosh, A., Hendry, H.J., 2001. Chloride-bromide- $\delta^{11}\text{B}$ systematics of a thick clay-rich aquitard system. *Water Resources Research* 37 (5), 1437–1444.
- Vengosh, A., De Lange, G.J., Starinsky, A., 1998. Boron isotope and geochemical evidence for the origin of Urania and Bannock brines at the eastern Mediterranean: effect of water–rock interactions. *Geochimica et Cosmochimica Acta* 62 (19–20), 3221–3228.
- Vengosh, A., Kloppmann, W., Marei, A., Livshitz, Y., Gutierrez, A., Banna, M., Gueppot, C., Pankov, I., Raanan, H., 2005. Sources of salinity and boron in the Gaza strip: natural contaminant flow in the Southern Mediterranean coastal aquifer. *Water Resources Research* 41, W01013. doi:10.1029/2004WR003344.
- Whittemore, D.O., 1988. Bromide as a tracer in ground-water studies: geochemistry and analytical determination. In: *Proceeding of the Ground Water Geochemical Conference*. Denver National Water Well Association, Dublin, OH, pp. 339–360.
- Wilkinson, J., Reynolds, B., Neal, C., Hill, S., Neal, M., Harrow, M., 1997. Major, minor and trace element composition of cloud-water and rainwater at Plynlimon. *Hydrology and Earth System Sciences* 1 (3), 557–569.
- Wood, W.W., Sanford, W.E., 1995. Chemical and isotopic methods for quantifying ground-water recharge in a regional, semi-arid environment. *Ground Water* 33 (3), 458–468.
- Yvon-Lewis, S.A., Butler, J.H., 2002. Effect of oceanic uptake on atmospheric lifetimes of selected trace gases. *Journal of Geophysical Research* 107 (D20), 4414. doi:10.1029/2001JD001267.