

Atmospheric chloride deposition in continental Spain

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Abstract:

The atmospheric bulk deposition rate of chloride in continental Spain was studied to get basic information in order to help in the evaluation of diffuse recharge to aquifers through an environmental chemical balance. Both new, recent data and bibliographic data have been used. Most sampling records are less than 5 years long and often only 1 year long. This means that the calculated mean yearly bulk deposition rate of chloride is quite uncertain by 30% on average, and larger than the values derived from records up to 15 years long. A map of atmospheric bulk deposition of chloride has been drawn using ordinary kriging. The mean bulk deposition rate of chloride varies from 1 to 30 g m⁻² year⁻¹ in coastal areas, with strong negative landward gradients between 0.1 and 1 g m⁻² year⁻¹ km⁻¹. In the centre of the Iberian Peninsula, chloride deposition rates vary from 0.2 to 0.5 g m⁻² year⁻¹, with gradients around or less than 5 × 10⁻³ g m⁻² year⁻¹ km⁻¹. The coefficient of variation of the mean bulk atmospheric deposition rate of chloride, for any place, ranges from 0.1 to 1. Values larger than ~0.5 are not a good indicator of natural uncertainty for this series of data that has a skewed distribution. The map of bulk deposition rate and its error is one of the terms needed for aquifer recharge estimation by means of the chloride ion balance. Copyright © 2008 John Wiley & Sons, Ltd.

KEY WORDS atmospheric deposition; chloride; spatial interpolation; continental Spain; recharge

Received 21 March 2007; Accepted 1 November 2007

INTRODUCTION

The study of the average chemical composition of atmospheric bulk deposition is the key to explaining the concentration of certain major ions in young groundwater and to estimating the average diffuse recharge to aquifers from rainfall through a chemical balance of predominantly atmospheric conservative constituents (Eriksson and Khunakasem, 1969; Richter *et al.*, 1983; Wood and Sanford, 1995; Custodio, 1997; Iglesias *et al.*, 1997). The chloride ion (Cl⁻) is ideal to perform chemical balances, since there is no significant long-term exchange with the environment, it is chemically stable, highly soluble, has a known origin in most cases and its accurate measurement is relatively easy and cheap using simple analytical methods (Feth, 1981). Recent studies (Öberg, 2003; Öberg and Sandén, 2005; Bastviken *et al.*, 2007) show that Cl⁻ interacts with soil organic matter through inorganic and biological processes and, thus, can be temporarily retained. But this means at most a delay of a few months for inorganic sorption and a few weeks for biological uptake. This is irrelevant for long-term aquifer recharge estimation (Scanlon *et al.*, 2006; Minor *et al.*, 2007). If there is recharge then there is no Cl⁻ loss, since it does not form stable minerals or significant quantities of organochlorine compounds.

The atmospheric bulk deposition includes solutes dissolved in precipitation (wet deposition) and solutes from atmospheric dust and aerosol settling (dry deposition).

The deposition rate is the areal flux of an atmospheric solute deposited per unit time. It is given by $A = PC_P$ (e.g. in grams per square metre per year for average yearly values), where P (mm) is the accumulated or mean precipitation during that period and C_P (g l⁻¹) is the mean concentration of the solute in the atmospheric bulk deposition. It is assumed that all atmospheric Cl⁻ deposited is in the form of the monovalent chlorine anion (Feth, 1981). Rain collectors may miss a part of Cl⁻ in gaseous form or in microparticles, since they settle slowly, but this effect is neglected here, and at most introduces a small systematic bias.

Global generation and distribution of atmospheric Cl⁻ and other ions of marine origin on the continent depends on the frequency and intensity of cyclonic activity in terrestrial mid-latitudes (Eriksson, 1960; Li, 1992). Once Cl⁻ is suspended in the atmosphere it can be carried inland by winds. Atmospheric Cl⁻ availability decreases along the wind-path with increasing distance from the ocean, resulting in higher Cl⁻ deposition rates near the coast than inland (Richter *et al.*, 1983; Gustafsson and Hallgren, 2000; National Atmospheric Deposition Program (NADP)/National Trends Network, 2000). Other factors, such as relief, wind speed and intensity, sampling time, vegetative cover, closeness to cities and industrial centres, mining facilities, etc., can act at a regional or local scale, modifying local bulk deposition of Cl⁻ (Martens *et al.*, 1973; Löye-Pilot and Morelli, 1988; Custodio, 1997; Gustafsson and Hallgren, 2000). Bulk deposition of Cl⁻ measured in any given place is determined by factors acting at different spatial scales and it is a characteristic value, provided there is no change

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in the climate and landscape. Comparison with other observation points allows the mapping of its distribution.

Historically, the main purpose of studies on the spatial distribution of atmospheric Cl^- deposition has been to monitor atmospheric quality to determine its impact on surface water and groundwater, and to assess soil acidification, corrosion near the coast, etc. (Löye-Pilot and Morelli, 1988; Carratalá *et al.*, 1998; Gustafsson and Hallgren, 2000; Feliu *et al.*, 2001). Other studies have produced or used existing atmospheric Cl^- deposition maps as key information for estimating recharge to aquifers by rain based on the balance of Cl^- (Eriksson and Khunakasem, 1969; Claassen and Halm, 1996; Sami and Hughes, 1996; Custodio, 1997; Iglesias *et al.*, 1997; Minor *et al.*, 2007).

The goal of this paper is to find the spatial distribution of the average yearly atmospheric bulk Cl^- deposition rate in continental Spain together with a measure of variability, such as the coefficient of variation. These data are needed for later calculation of the rate of recharge by rain to aquifers based on the environmental chemical balance. This paper refers only to peninsular Spain. So it does not refer to insular Spain (the Balearic Islands and the Canary Islands), where the density of data does not allow proper mapping.

CLIMATE AND OROGRAPHIC CONTROLS ON THE IBERIAN PENINSULA

The Iberian Peninsula is located in southwest Europe, between latitudes 36° and 44°N (Figure 1), under the dominant influence of air masses originating in the North Atlantic and the tropical Atlantic Ocean effect (Font, 1983; MIMAM, 2000). Owing to the relatively high elevation of continental highlands (mesetas; about 900 m a.s.l. in the northern half and about 700 m a.s.l. in the southern half), encased in mountain ranges, a substantial

part of peninsular Spain is characterized by continental climate, with hot and dry summers, and cold and to some extent humid winter–spring seasons. Recurrent dry spells, extending from 2 to 5 years, have been recorded, with alternating wet and dry periods linked to the North Atlantic oscillation.

The highest precipitation happens usually in late autumn and winter, when there are several days of regular precipitation associated with two main meteorological patterns. The first is characterized by a high-pressure atmospheric situation over the Azores Islands and a pronounced depression over the British Isles that generate a circulation of cold air masses from the North Atlantic. The second is associated with deep lows initially located over Gulf of Cadiz that travel slowly eastward and generate a circulation of air masses from the subtropical Atlantic. The eastern coast of continental Spain at that time receives precipitation from western Mediterranean wet air masses, which is generally limited to short distances from the coastline. Convective rains can produce heavy storms, especially in summer and early autumn; these represent less than 10–15% of the annual precipitation in these areas (Font, 1983; MIMAM, 2000), but capable of producing floods and significant for recharge after soil water deficit is satisfied.

The mean precipitation ranges from 2000 mm year^{-1} in western and northern coastal areas, to about $500\text{--}600\text{ mm year}^{-1}$ over the North Meseta and $380\text{--}500\text{ mm year}^{-1}$ in the South Meseta. Precipitation is less than 300 mm year^{-1} in southeast Mediterranean coastal areas, where a semi-arid climate condition exist (Font, 1983; MIMAM, 2000).

DATA ACQUISITION

Through this paper, chloride (Cl^-) deposition is the weight of Cl^- per unit surface area, and refers to a given



Figure 1. Geographical location of the Iberian Peninsula, showing the main mountain ranges, hydrographic basins and some places mentioned in the text. Shading shows ranges of altitude from lighter (sea level) to darker (up to more than 2000 m a.s.l.)

time interval. The deposition rate is the deposition per unit of time, here taken as a year. Bulk deposition, or simply deposition if unspecified, is the total (wet plus dry) deposition. Wet deposition refers to Cl^- content in rainfall water (measured by means of samplers that only open when there is rain) and dry deposition refers to Cl^- directly deposited on the land surface in the form of dust or atmospheric aerosols. Bulk rain samplers are continuously open to the atmosphere and are assumed to sample bulk deposition, although they may fail to collect settling atmospheric aerosols properly. This effect is neglected, since it is assumed small and at most introduces a small bias.

Deposition is symbolized D and deposition rate as A . An overbar means mean values. Mean yearly deposition rate is symbolized \bar{A} , and the mean over the whole sampling period \bar{A}^* . The coefficient of variation (CV) for any variable is the dimensionless ratio of the standard deviation to the mean value. It is given as a fraction.

For characterization of the saline contribution from precipitation, and the effect of sampling frequency and methodology, a set of stations was installed. Ion chromatography was used to improve the measurement of the low mineral concentrations that are common in precipitation water. In addition, an intensive search for existing published information yielded 192 sets of bulk, wet and dry Cl^- deposition data measured at 185 different geographic points (Figure 2).

Atmospheric chloride deposition at the IGME rainfall sampling stations

New bulk Cl^- deposition data were generated by 14 rain-gauges installed by the authors and operated by the Geological Survey of Spain (IGME), and one rain-gauge operated by the Technical University of Catalonia (UPC). Standard and simple rain samples have been used. All rainfall samples were analysed at the IGME Laboratory in Tres Cantos, Madrid (Alcalá and Custodio, 2004).

These 15 rain-gauges collected rainfall that accumulated during periods of time of around 1 month. At the end of each period, the sample obtained included the volume of rainfall and a known volume of distilled water added to rinse the 320 mm diameter collector funnel. The Cl^- concentration C in rain during each period sampled is

$$C = C'V(V - W) \quad (1)$$

and rainfall depth is

$$P(\text{mm}) = 10^{-3} \frac{V - W}{S_C} \quad (2)$$

where C' (g l^{-1}) is the Cl^- concentration in the sample, S_C (m^2) is the collector funnel area, V (ml) is the water volume and W (ml) is the volume of distilled water added.

The mean bulk deposition rate of Cl^- (Table I, column a) is

$$\bar{A}^* (\text{year}^{-1}) = 365 \frac{\sum_{i=1}^n A_i}{\sum_{i=1}^n \Delta t_i} \quad (3)$$

where n is the number of sampling periods at the station and Δt_i is the length of time of the corresponding sample. This allows the consideration of discontinuous data series.

The regularity of yearly values of the bulk deposition at any sampling site during the sampling period is evaluated through the dimensionless value a_i (for period i of duration Δt_i (days)):

$$a_i = 365 \frac{D_i / \Delta t_i}{\bar{A}^*} \quad (4)$$

a_i varies around 1.0 when the deposition tends to be uniform in time, with fluctuations due to seasonal variations (Table I, column b).

Atmospheric chloride deposition at the EMEP network stations

The Cooperative Programme for Monitoring and Evaluation of Long-Range Transmission of Air Pollutants in Europe (EMEP: <http://projects.dnmi.no/~emep/>) includes several different stations that sample precipitation for later analysis of most of them. These stations have chemical rainfall data covering long time periods, so time variability of Cl^- deposition can be calculated. The sampling protocols and chemical analysis procedures are described in EMEP (1996) and Alcalá (2006). Precipitation data and chemical analyses were taken from the meteorological datasets at 15 Spanish stations, three French stations and three Portuguese stations (Figure 2). Portuguese and French stations were included to help defining the Cl^- deposition within the boundaries of peninsular Spanish territory. The Spanish and French stations sample wet deposition in automatic rain-gauges and the Portuguese stations sample bulk deposition in conventional open rain-gauges.

Since not all rainfall events collected at the stations were analysed, this poses difficulties to find the yearly Cl^- deposition rate by simple accumulation of partial deposition values along the year. This is more accentuated in the first years of station's operation and in the last year if sampling does not cover the full year.

For a certain time period (e.g. 1 day) the deposition is D (g m^{-2}) = PC , where P (mm) is the precipitation in that period and C (g l^{-1}) is the Cl^- concentration in the cumulative water sample after correcting for the addition of distilled water after Equation (1). But not all of the days with precipitation have the corresponding P and/or C values. When the rainfall from successive several days is accumulated and analysed as a single sample, D is the deposition for that set of days.

Table I. Geographic location, operating period and mean bulk Cl^- deposition rate \bar{A}^* from the IGME rainfall sampling network (data units: $\text{g m}^{-2} \text{ year}^{-1}$)

Station ^a	IGME code	Coordinates	Elevation (m a.s.l.)	Sampling period		a ^b		b ^c		
				From	To	n	\bar{A}^*	n	\bar{A}^*	a_i
Quintana*	01	43°22'N 5°31'W	377	28 Feb 2001	2 Aug 2002	521	3.4	491	2.8	0.89
Cuenca*	02	40°03'N 2°07'W	998	3 Mar 2001	1 Jul 2002	479	0.3	449	0.2	1.17
Sierra de Vicort*	03	41°22'N 1°29'W	1383	4 Mar 2001	2 Aug 2002	515	0.4	485	0.3	0.94
El Casar*	04	40°42'N 3°25'W	831	22 May 2001	12 Jul 2002	416	0.5	386	0.4	0.95
Siete Aguas	05	39°29'N 0°54'W	799	28 Feb 2001	31 Jul 2002	521	1.0	521	1.0	1.30
La Bastida*	06	40°34'N 6°03'W	1114	28 Feb 2001	6 Sep 2002	556	0.5	526	0.4	1.34
Huerta del Rey*	07	41°50'N 3°20'W	1007	28 Feb 2001	19 Sep 2002	570	0.5	540	0.4	1.32
Peñarroya*	08	38°18'N 5°16'W	577	28 Feb 2001	30 Sep 2002	579	0.7	549	0.5	1.05
Santiago*	09	42°52'N 8°31'W	285	17 Feb 2001	10 Aug 2002	569	4.3	566	3.9	1.75
University of Almería	10	36°50'N 2°23'W	20	2 Feb 2001	30 Aug 2002	574	5.3	574	5.3	0.77
Dehesas de Guadix	11	37°35'N 3°06'W	674	30 Jan 2001	29 Aug 2002	578	1.4	578	1.4	0.98
Doñana	12	36°59'N 6°26'W	5	30 Nov 2000	27 Dec 2001	235	1.2	235	1.2	0.66
San Pablo	13	39°33'N 4°21'W	917	10 Oct 2002	10 Nov 2003	396	0.6	396	0.6	1.21
Roquetes	14	40°49'N 0°30'W	50	16 Oct 2002	4 Nov 2003	384	1.1	384	1.1	0.95
Barcelona	15	41°23'N 2°06'E	125	1 Mar 1999	4 Apr 2003	1495	4.0	1495	4.0	0.92

^a Stations marked by an asterisk have \bar{A}^* estimated by omitting anomalous early samples in column 'b'.^b \bar{A}^* estimated from all samples; n is the number of days with a continuous precipitation record analysed.^c n is the number of days with a continuous precipitation record analysed. \bar{A}^* estimated by omitting anomalous early samples at stations marked with asterisk. σ is the standard deviation and p_{10} and p_{90} are the 10th and 90th percentiles of a_i (partial values of bulk deposition A_i respect to the yearly bulk deposition \bar{A}^*).

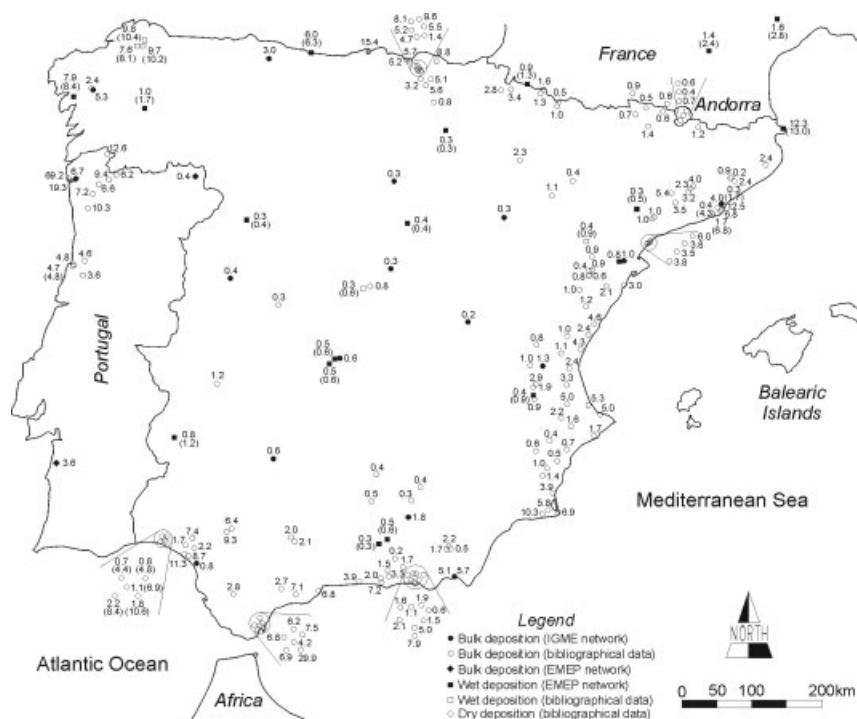


Figure 2. Geographical location of IGME rainfall sampling stations, EMEP network stations and other data from the literature used in this paper. Original bulk, wet and dry Cl^- deposition rates are in $\text{g m}^{-2} \text{year}^{-1}$. In parentheses are the EMEP network wet deposition data and the wet and dry deposition rate data from the literature after adjusting to an equivalent value of bulk Cl^- deposition rate in $\text{g m}^{-2} \text{year}^{-1}$ using the approaches given in the text

The total deposition is

$$D^T = \sum_i D_i^M + \sum_j D_j^E = D^M + D^E \quad (5)$$

where D_i^M is the known deposition at a measured period and D_j^E is the unknown deposition during a non-measurement period.

Assuming that all of the significant precipitation is recorded:

$$P^T = \sum_i P_i^M + \sum_j P_j^E = P^M + P^E \quad (6)$$

D^T is estimated assuming proportionality with precipitation in the periods with and without deposition data:

$$D^T = \frac{P^T}{P^M} D^M \quad (7)$$

There are other possibilities to improve the estimation, but they have not been considered here because the proportional correction is assumed to be enough for this study.

A_i is Cl^- deposition calculated at each station for each natural year with data. For a series with several values of A_i , the mean value of the set is \bar{A} (Table II, column a). \bar{A} is assumed to be an estimation of \bar{A}^* , the yearly mean value calculated from long time-series (Table II, column b). σ_{A_i} is the standard deviation of \bar{A} , which gives a measure of the yearly variability of A plus the error of estimation due to corrections to take into account incomplete series (Table II, column a). If the A_i values

can be assumed to be normally distributed, then σ_{A_i} can be expressed as (Davis, 1986)

$$\sigma_{A_i}^2 = \sigma_A^2 + \sigma_{d_i}^2 \quad (8)$$

where σ_A is the yearly standard deviation of \bar{A} and σ_{d_i} is the standard deviation of the error introduced in the calculation of \bar{A} due to incomplete series in a given station. A minimum value of σ_A can be estimated using Equation (8) once σ_{d_i} at each station is calculated. The value of σ_{d_i} has been estimated by selecting natural years in several stations where all precipitation was analysed. Each natural year provides a value of A_i . By randomly suppressing 10% of the data, a new shortened series is obtained. The process is repeated N times (for example 500) and N shortened series are obtained and the A_i values calculated by proportional interpolation as explained above. This provides new values of A_i that differ from the measured value, A_i . The difference between both values is an evaluation of d_i . The values of d_i from the different stations present a normal distribution, and their standard deviation σ_{d_i} is around $0.077 \text{ g m}^{-2} \text{year}^{-1}$.

The coefficient of variation of \bar{A} (CVA) for all stations is between 0.04 and 0.64, with an average value around 0.40 (Table II, column a). For the detailed procedure to find \bar{A} , σ_{d_i} and the other parameters described for each station, see Alcalá (2006).

\bar{A} was checked to get additional spatially distributed information. The original sources of these data can be found in Alcalá (2006).

Station	EMEP code	Coordinates	Elevation (m a.s.l.)	Sampling period		Deposition type	a ^b			b ^c		%(\bar{A}^*/\bar{A}) ^d										
				From To			CVA	\bar{A}	σ_{PT}	ρ^M	σ_T		$\sigma_{\bar{A}}$	D^M	\bar{A}^*							
				i	j											p^T	σ_{PT}	Mean	Median	a_i	p_{10}	p_{90}
San Pablo	ES01	39°33'N 4°21'W	917	1 Jan 1985	31 May 2003	Wet	19	649	244	604	0.5	0.2	0.46	0.96	0.85	0.38	0.60	1.36	6523	8.2	0.5	-6.61
La Cartuja ^a	ES02	37°12'N 3°36'W	720	1 Jan 1987	12 Nov 1995	Wet	9	300	100	281	0.3	0.2	0.57	1.00	0.80	0.55	0.65	1.51	3207	2.4	0.3	-4.84
Roquetes	ES03	40°49'N 0°30'W	50	1 Jun 1987	31 May 2003	Wet	17	432	125	387	0.8	0.3	0.39	1.03	0.91	0.35	0.64	1.47	5642	11.6	0.8	-3.03
Logroño ^a	ES04	42°27'N 2°21'W	370	1 Mar 1988	31 Dec 2000	Wet	13	415	92	398	0.3	0.1	0.22	1.04	1.00	0.22	0.78	1.36	4689	4.2	0.3	-3.02
Noia	ES05	42°44'N 8°55'W	685	1 Jan 1993	30 May 2000	Wet	8	1688	780	1611	7.9	4.5	0.57	0.98	0.93	0.39	0.52	1.43	2554	60.7	8.7	9.41
Viznar	ES07	37°14'N 3°28'W	1230	1 Nov 1995	30 Sep 2003	Wet	9	594	282	324	0.5	0.2	0.40	1.07	1.04	0.39	0.71	1.55	2891	4.5	0.6	12.10
Niembro	ES08	43°26'N 4°51'W	134	1 Jan 1999	30 Sep 2003	Wet	5	666	253	652	6.0	1.9	0.32	1.00	1.03	0.29	0.74	1.28	1734	29.2	6.2	3.13
Campisabalos	ES09	41°16'N 3°08'W	1360	1 Jan 1999	31 Dec 2003	Wet	5	427	73	416	0.4	0.1	0.19	1.00	0.96	0.13	0.91	1.13	1734	2.0	0.4	2.44
Cap de Creus ^a	ES10	42°19'N 3°19'E	23	1 Jan 1999	31 Dec 2000	Wet	2	273	79	258	12.3	0.4	0.04	1.00	1.00	0.04	0.98	1.02	731	23.2	11.6	-5.47
Barcarrota	ES11	38°28'N 6°55'W	393	1 Mar 1999	30 Sep 2003	Wet	5	471	159	449	0.8	0.3	0.32	0.98	0.86	0.22	0.80	1.22	1672	3.9	0.9	4.54
Zorra	ES12	39°05'N 1°06'W	885	1 Jan 1999	30 Sep 2003	Wet	5	301	78	287	0.4	0.2	0.35	0.98	0.97	0.28	0.73	1.734	2.0	0.4	0.75	
Peláusende	ES13	41°17'N 5°52'W	985	1 Aug 2000	30 Sep 2003	Wet	4	300	54	298	0.3	0.1	0.17	1.10	0.91	0.42	0.86	1.49	1157	1.1	0.4	25.30
Els Torms	ES14	41°23'N 0°43'E	470	1 Nov 2000	30 Sep 2003	Wet	4	179	73	177	0.3	0.1	0.48	1.06	1.04	0.17	0.92	1.23	1065	1.0	0.3	36.20
Risico Llano	ES15	39°31'N 4°21'W	1241	15 Oct 2000	31 Aug 2003	Wet	4	346	205	343	0.5	0.3	0.64	1.13	1.10	0.62	0.57	1.71	1018	2.1	0.8	42.10
O Saviñao	ES16	42°38'N 7°42'W	506	1 Mar 2001	30 Sep 2003	Wet	3	629	152	625	1.0	0.4	0.42	0.98	0.96	0.28	0.76	1.21	945	2.9	1.1	14.90
Bragança	PT01	41°49'N 6°46'W	691	1 Jan 1989	31 Dec 2000	Bulk	11	576	254	512	0.4	0.2	0.52	0.93	0.96	0.30	0.68	1.16	4018	3.8	0.3	-15.70
Viana do Castelo	PT03	41°42'N 8°48'W	16	1 Jan 1989	31 Dec 2000	Bulk	12	1342	337	1250	6.7	2.3	0.34	0.99	1.03	0.49	0.36	1.34	4383	75.0	6.3	-7.04
Monte Velho	PT04	38°05'N 8°48'W	43	1 Sep 1989	31 Dec																	

Percentage of variation between \bar{A}^* (column 'b') and \bar{A} (column 'a').

Most of the Cl^- deposition data from the literature was found as average precipitation times average Cl^- content, and only in a few cases are the results from cumulative, successive sampling of deposition during at least 1 year. There are differences among both methods, since the deposition obtained from mean precipitation and Cl^- average content does not usually consider light rains with high saline content or dry deposition during dry spells.

ANALYSIS OF DATA

Bulk Cl^- deposition values generated at IGME-operated rainfall stations and EMEP network stations were checked at seasonal and yearly time-scales respectively to see whether they were representative of the environmental conditions at each site. The regularity of partial values of Cl^- deposition during the study period at stations was studied through the a_i values by using Equation (4).

Some IGME stations show very high initial values of a_i , due probably to sampling errors, an uncertain knowledge of the date when sampling started, or the collector was not clean. Therefore, these data were omitted from all stations where they appeared, and the \bar{A}^* values were recalculated (Table I, column b). Other occasional anomalous values of a_i obtained at some stations are related to very high precipitation or very high Cl^- content, or both at the same time, causing very high or very low bulk deposition values. These values are part of the heterogeneity of the deposition at each site and have to be taken into account (Table I, column b). They affect the mean value. The rest of the values of a_i show seasonal changes that are more or less coincident to all stations.

At EMEP network stations, for yearly values of Cl^- deposition rate A_i , a_i varies between 0.3 and 2.5, with the most frequent range being between 0.7 and 1.3 (Table II, column a). At the stations with the longest wet Cl^- deposition records, a certain variation in a_i over a period of ~ 4 years is observed (Table II, column a). At stations PT01 and PT03, which sample bulk Cl^- deposition, this periodicity cannot be seen so clearly, since a certain increasing trend of a_i is observed in the final years. This

could be associated with possible inclusion of Cl^- being not strictly derived from marine aerosols.

The EMEP network stations have relatively long records that allow quantification of the difference among the Cl^- deposition rate estimation procedures and, at the same time, characterize this variation according to the length of the study period. In this case, the yearly deposition rate \bar{A} can be calculated as the mean value of yearly deposition A_i (Table II, column a), or by Equation (7) from the measured Cl^- deposition for the whole recording period \bar{A}^* (Table II, column b). Depending on the calculation procedure, differences between $\pm 1\%$ and $\pm 40\%$ in the calculation of \bar{A} may be found for stations with 1- to 5-year records (Table II, column c). The differences are reduced to values between $\pm 1\%$ and $\pm 15\%$ for sampling periods of around 10 years or longer.

In a few places in the Iberian Peninsula the bulk, wet and/or dry Cl^- deposition has been measured at the same time for several years: La Castanya, Barcelona; Sierra de los Filabres, Almería; Aveiro, NW Portugal; Bilbao; Barcelona; Madrid; Morella, Castellón (Alcalá, 2006). They show that dry Cl^- deposition rate varies between 1% and 40% of the bulk deposition rate. In semi-arid and coastal zones, where atmospheric dust may be a significant contribution to bulk deposition, the difference may be over $\pm 40\%$ for short records. The difference is also high for inland stations at high altitude with short records. The differences between the methods are not enough to discard the bulk deposition values obtained from mean precipitation and Cl^- content in rainfall samples, although the results have a greater degree of uncertainty.

To use dry and wet Cl^- deposition rates found in the literature and the wet Cl^- deposition rates calculated at the EMEP network stations as indicative values of bulk Cl^- deposition, a numerical conversion criterion based on the differences measured between wet and bulk deposition at the same place was applied. Characteristic qualitative coefficients of conversion have been found for the main geographic domains in the Iberian Peninsula, with different weather, orography, etc. (Table III). For original data see Alcalá (2006). Comparison for the

Table III. Weighting coefficients of conversion (they add to unity) or proportions that represent the wet and dry Cl^- deposition within the bulk Cl^- deposition in the main geographic domains considered in continental Spain

Main geographic domains considered in continental Spain	Main saline influence	Weighting coefficient ^a	
		Wet	Dry
N and NW coastal zones	Atlantic Ocean	0.95–0.99 (0.97)	0.01–0.05 (0.03)
N and NW high mountain zones	Atlantic Ocean	0.60–0.65 (0.62)	0.35–0.40 (0.38)
Inland zones	Atlantic Ocean	0.80–0.95 (0.90)	0.05–0.20 (0.10)
S and SW coastal zones	Atlantic Ocean	0.70–0.85 (0.78)	0.15–0.30 (0.22)
NE and E coastal zones	Mediterranean Sea	0.75–0.85 (0.79)	0.15–0.30 (0.21)
S and SE coastal zones	Mediterranean Sea	0.50–0.70 (0.63)	0.30–0.50 (0.37)
S and SE high mountain zones	Mediterranean Sea	0.70–0.80 (0.75)	0.20–0.30 (0.25)
Urban and industrial areas	Pollution	0.70–0.90 (0.76)	0.10–0.30 (0.24)

^a Average values in parentheses.

same yearly monitoring data period in different years, in different study periods and with different calculation procedures increases the uncertainty and makes it necessary to assign different degrees of confidence to the data from each available information source. This adjustment is considered qualitative and only indicative of their order of magnitude.

An example to find quantitative conversion criteria was the comparison carried out between bulk and wet Cl^- deposition recorded from November 2002 to November 2003 at the San Pablo and Roquetes EMEP network stations (Figure 1), which usually sample only wet deposition. To do this, a bulk atmospheric deposition collector was installed at each station.

San Pablo is a typical station representative of continental areas and Roquetes is a station typical of the Mediterranean coastal zone, but at some distance from the coast. The wet Cl^- deposition rates at San Pablo and Roquetes during the mentioned period were $0.45 \text{ g m}^{-2} \text{ year}^{-1}$ and $0.76 \text{ g m}^{-2} \text{ year}^{-1}$ respectively. These values are within the long term yearly ranges at both stations, found to be $0.49 \pm 0.23 \text{ g m}^{-2} \text{ year}^{-1}$ and $0.75 \pm 0.29 \text{ g m}^{-2} \text{ year}^{-1}$ respectively (Table II, column a). The respective wet Cl^- depositions are 80% and 70% of bulk Cl^- deposition (calculated as $0.56 \text{ g m}^{-2} \text{ year}^{-1}$ and $1.09 \text{ g m}^{-2} \text{ year}^{-1}$ at San Pablo and Roquetes respectively) during this period (Table I, column b). The difference is due to Cl^- deposited by atmospheric dust and aerosols.

The stations with time-series of 2 years or longer have allowed us to find a value of natural variability in the mean yearly bulk Cl^- deposition rate which has been expressed in relative terms by means of the coefficient of variation (Figure 3). The natural variability found from

short time-series (data from the IGME stations and most of the data from the literature) is only an approach to what was measured at the EMEP network stations with long time-series. Comparing data for large areas of continental Spanish territory, compiled on different dates, with different sampling periods and of different types (wet and bulk Cl^- deposition), leads to noticeable uncertainty which rarely has been estimated. Data are considered good when the datasets comprise several decades and only an approach to the order of magnitude when the series record is only 2 or 3 years.

The scarce data from the literature shows that coefficients of variation for bulk Cl^- yearly deposition rates are usually between 0.01 and 0.3 of the wet Cl^- deposition rate measured at the site, with an average of ~ 0.1 (Figure 3). This is justified by the randomness of precipitation compared with the usually more regular dry Cl^- deposition rate at any given place in the same time interval.

SPATIAL ANALYSIS OF THE BULK CHLORIDE YEARLY DEPOSITION RATE

Methodology

Mapping of Cl^- deposition was carried out through spatial interpolation of data by using geostatistical tools. Geostatistical methods are based on the theory of the spatial random function concept, which considers each observation as the result of a random process at that point. The most common method of spatial interpolation is ordinary kriging, although there are others methods, such as the weighting of values by the inverse of distance, which was also applied but not shown here.

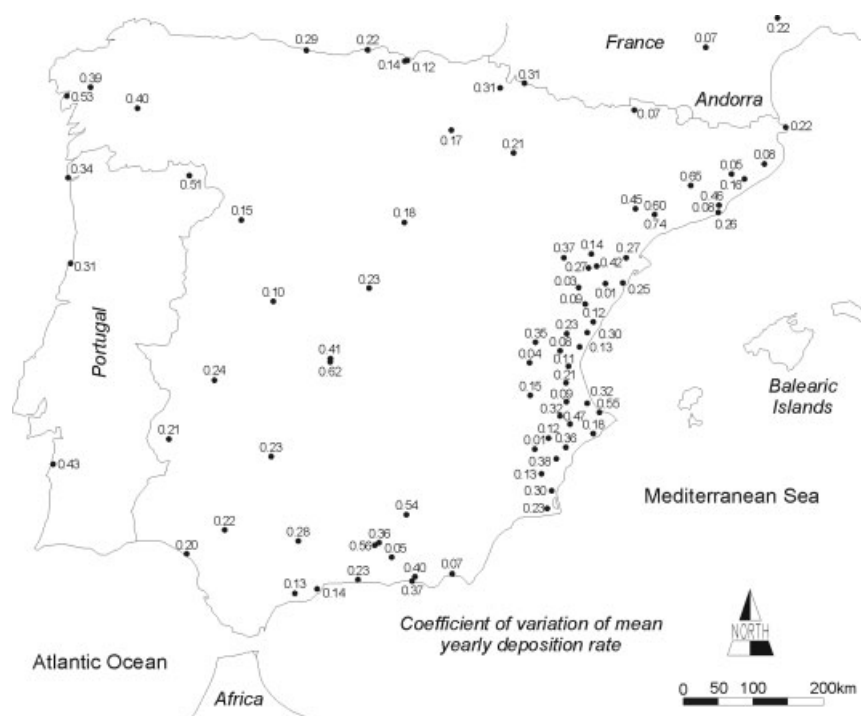


Figure 3. Coefficient of variation of bulk Cl^- deposition rate in continental Spain

Ordinary kriging makes it possible to estimate Z_A , the value of a variable Z at point A , by means of a simple mathematical expression of spatial correlation from available data (Matheron, 1971):

$$Z_A = \sum_{i=1}^n \lambda_i Z_i \quad (9)$$

where λ_i is the weight assigned to a measurement Z_i at sampling point i and n is the total number of point data. The λ_i values are calculated from the spatial distribution of data and the semi-variogram, which is a measure of spatial correlation:

$$\gamma(h) = \frac{\sum_{i=1}^{N(h)} [z(x_i) - z(x_i + h)]^2}{2N(h)} \quad (10)$$

where $N(h)$ is the number of pairs of observations separated by a distance h and $z(x_i)$ is the value at point x_i .

Kriging uses the information contained in the semi-variogram to calculate the weight factors of the linear combination of neighbouring values (Isaaks and Srivastava, 1989), with the additional constraint that $\sum_{i=1}^n \lambda_i = 1$ at any point. Kriging provides the best linear unbiased estimator of the variable, as well as a measure of uncertainty, such as the standard deviation of the interpolation error (Matheron, 1971).

The experimental semi-variograms were calculated using the GAMV program within the GSLIB library (Deutsch and Journel, 1998). The estimator and the kriging standard deviation were found with the KT3D program. The VARIOWIN program (Pannatier, 1996) was used to fit the experimental semi-variogram manually to a theoretical semi-variogram model.

Specific assumptions

This general geostatistical approach to estimating bulk Cl^- deposition may be considered concise and conceptually correct, although in practice it deteriorates when data are poorly distributed in space (Milly and Eagleson, 1987). Ordinary kriging does not take into account the relationship between bulk Cl^- deposition and other external variables that partially control it, such as distance from the sea, altitude, orographic features and wind regime and intensity. They can be introduced by means of other types of kriging, which are not applied here.

To improve the estimation of the spatial distribution of bulk Cl^- deposition rate, large zones in the Iberian Peninsula have been considered where the variable tends to be homogeneous, such as large valleys, plains or mountain ranges (Table III). Local studies were used to find out or predict the variable behaviour in these zones. This procedure is similar to what Gustafsson and Hallgren (2000) did to define the behaviour of bulk Cl^- deposition in the three main geographic domains into which southern Sweden may be divided, or to what Richter *et al.* (1983), Li (1992) and National Atmospheric Deposition Program

(NADP)/National Trends Network (2000) did to define the behaviour of bulk Cl^- deposition on coastal and continental domains of the USA. The purpose was to characterize, and later quantify by geostatistical methods, the spatial distribution of the mean value and coefficient of variation of the bulk Cl^- deposition rate for a small dataset with a poor spatial distribution.

This way of limiting new bulk Cl^- deposition values to certain values similar to those in their geographic surroundings is an approach to assign secondary qualitative information (topography, distance from the sea, wind regime and intensity, etc.) to the variable which is to be interpolated. Similar approaches or rules have been proposed by Batjes (1996) for the estimation of pedological variables from hydrological and environmental variables.

Application

The measured and adjusted mean atmospheric bulk Cl^- deposition rate datasets were pooled together. The mean bulk Cl^- deposition rate (in grams per square metre per year) and its coefficient of variation have been considered as two different variables. Both variables have been spatially regionalized, separately, by ordinary kriging based on available data at the nodes of a regular grid with 4976 cells of $10 \text{ km} \times 10 \text{ km}$ covering the peninsular Spanish territory. In total, 192 data of average atmospheric bulk Cl^- deposition and 82 coefficients of variation were available (Table IV).

RESULTS

The univariate distribution of the mean values and coefficient of variation datasets follow a lognormal distribution (Figure 4). In both cases, the experimental semi-variogram roughly follows an omnidirectional fit to a theoretical spherical semi-variogram (Figure 5). The fit of the series of the logarithm of mean deposition rates yields a range of $\sim 124 \text{ km}$, a sill of 0.22 and a nugget of 0.03 (both in $\log |g \text{ m}^{-2} \text{ year}^{-1}|$). The fit of the series of the logarithm of the coefficients of variation provides a range of 11 km, a sill of 0.19 and a nugget of 0.07, in a poorly defined semi-variogram.

Previous studies of atmospheric Cl^- deposition in eastern continental Spain (Carratalá *et al.*, 1998) proposed fitting the experimental semi-variogram to a spherical model, with which they found a range of $\sim 110 \text{ km}$, a sill

Table IV. Descriptive statistics^a for the set of mean ($g \text{ m}^{-2} \text{ year}^{-1}$) and the coefficient of variation of atmospheric bulk Cl^- deposition rate in continental Spain

	<i>n</i>	<i>x</i>	σ	CV	Min.	<i>m</i>	Max.
Average (mean) value	192	3.81	3.98	1.04	0.21	2.40	29.9
Coefficient of variation	82	0.25	0.16	0.64	0.00	0.23	0.74

^a *n*: number of data; *x*: mean; σ : standard deviation; CV: coefficient of variation; *m*: median.

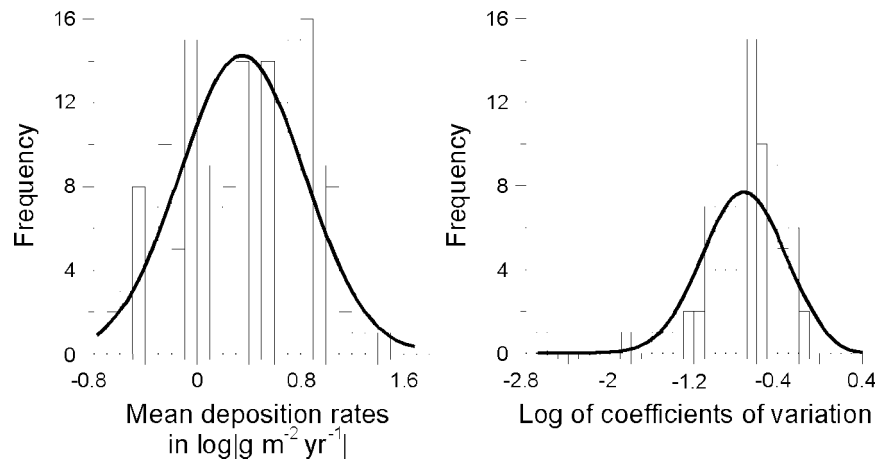


Figure 4. Logarithmic mean bulk Cl^- deposition rate and logarithmic coefficient of variation histograms. The corresponding lognormal density function has been overimposed

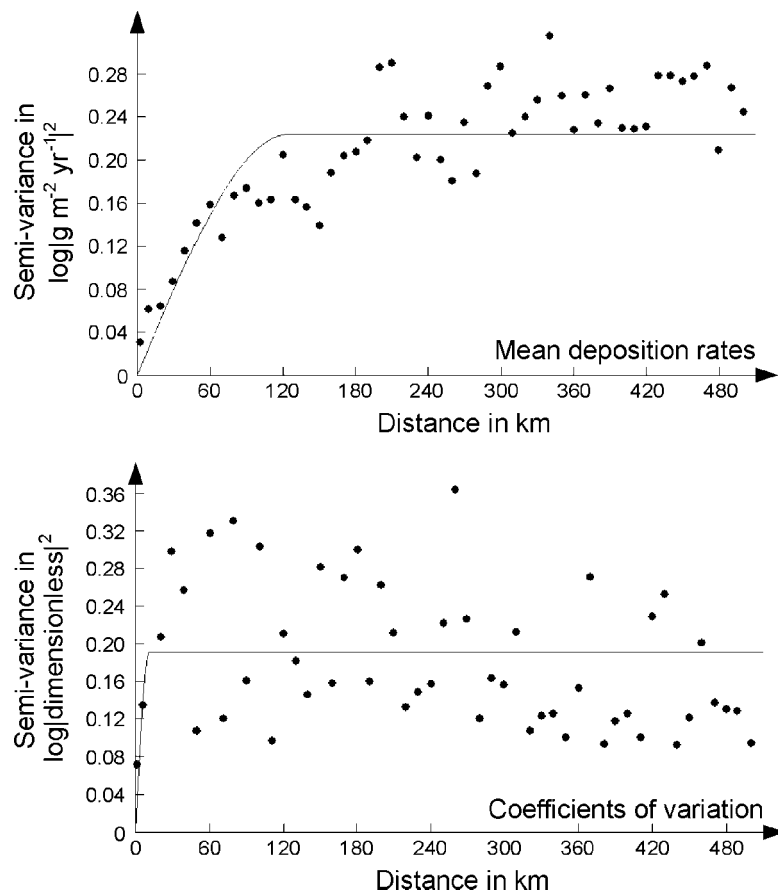


Figure 5. Experimental semi-variogram and theoretical spherical semi-variogram that best fit the series of average bulk deposition rates and coefficients of variation

of 0.65 and a nugget of 0.04 (both in $\log [\text{g m}^{-2} \text{ year}^{-1}]$). In a study on bulk Cl^- deposition in the south of Sweden, Gustafsson and Hallgren (2000) proposed fitting experimental semi-variograms to spherical or Gaussian models, or a combination of them. In that region, where there is less orographic variation than in Spain, a range of ~ 335 km, a sill of 1.05 and a nugget of 0.04 (both in $\log [\text{g m}^{-2} \text{ year}^{-1}]$) were found. Similar values have been reported by spatial Cl^- deposition estimates made in the USA (NADP, 2000).

The spatial distribution of mean deposition rates (Figure 6a) and the corresponding coefficients of variation (Figure 6b) datasets were mapped by spatial interpolation with ordinary kriging. Mean rainfall rate (Figure 6c) and Cl^- concentration in atmospheric bulk deposition (Figure 6d) are also mapped in order to show the dependence of both variables on atmospheric bulk Cl^- yearly deposition.

The gradients of territorial variation in the mean bulk Cl^- deposition rate (in grams per square metre per year

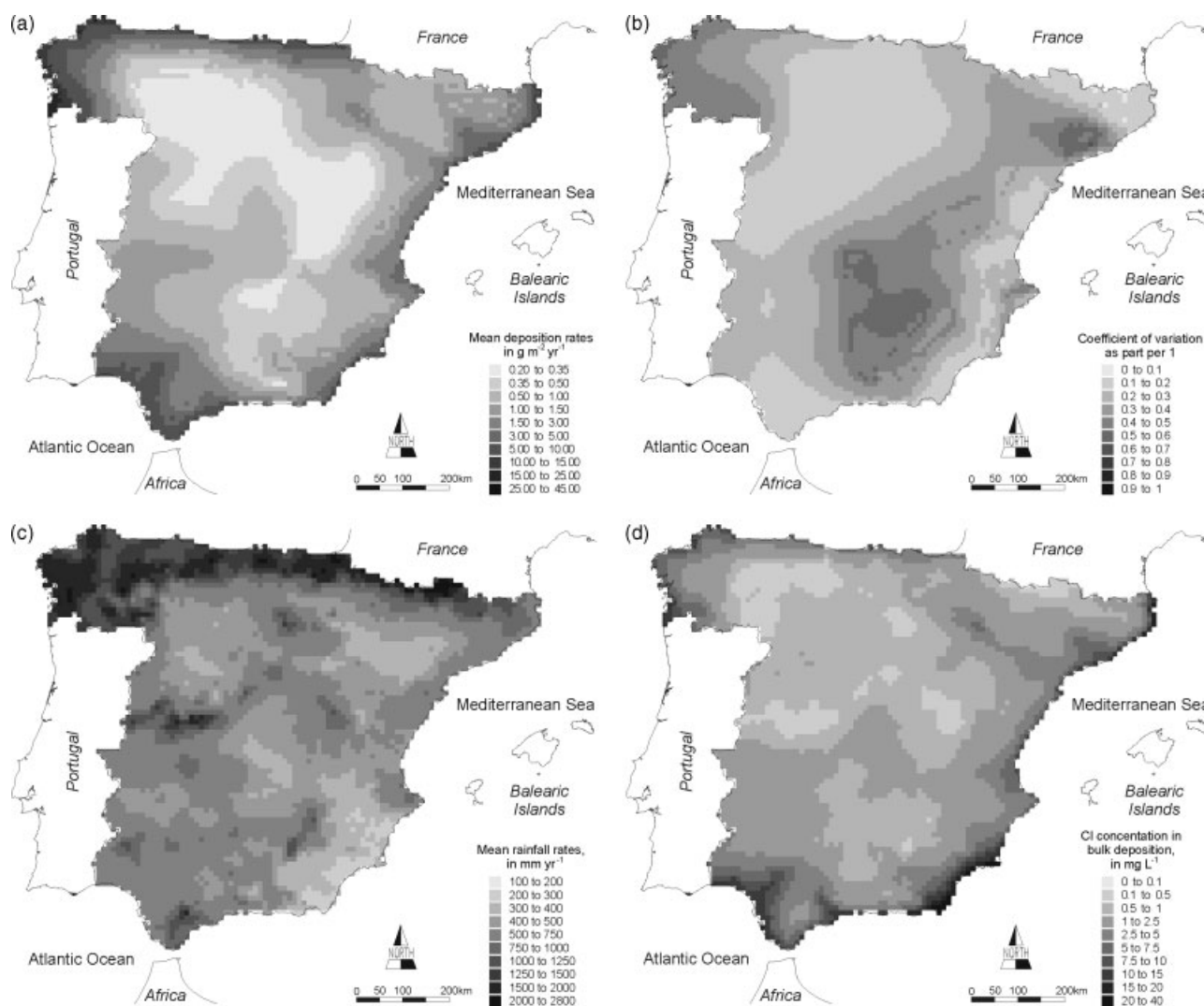


Figure 6. Bulk Cl^- deposition rate in continental Spain. (a) Map of mean value ($\text{g m}^{-2} \text{ year}^{-1}$). (b) Coefficient of variation map. (c) Mean rainfall rate (mm year^{-1}). (d) Cl^- concentration (mg l^{-1}) in bulk deposition. Values are discretized in cells of $10 \text{ km} \times 10 \text{ km}$

per kilometre) are calculated by dividing the bulk Cl^- deposition rates interpolated by ordinary kriging by the distance between them (Figure 7).

The kriging standard deviation for the mean values of bulk Cl^- deposition rate vary from $\sim 1 \text{ g m}^{-2} \text{ year}^{-1}$ in zones with sufficient measured data to $\sim 1.9 \text{ g m}^{-2} \text{ year}^{-1}$ in zones with scarce information (Figure 8a). These figures are an order of magnitude higher than the estimated deposition rates in continental highland zones without data and are half or one order of magnitude less than the estimated values in coastal zones with available data. The kriging standard deviation for the coefficient of variation dataset vary from ~ 1 in coastal zones with sufficient data to ~ 1.7 in inland zones with hardly any information (Figure 8b). These figures indicate a higher uncertainty of mean values estimation.

The geostatistical model was evaluated for both variables by comparing measured data $|z(x)|$ with data estimated by ordinary kriging $|z^*(x)|$ from the other points for the same geographical location (Figure 9). The comparison enables evaluation of the error introduced by the geostatistical model for each estimated value. The

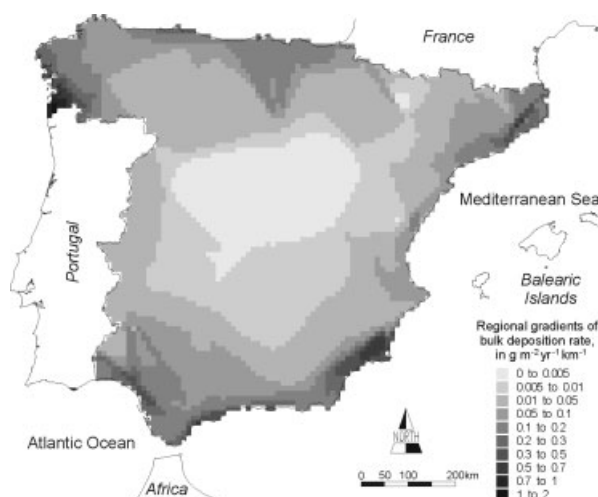


Figure 7. Regional gradients of bulk Cl^- deposition rate in continental Spain, in $\text{g m}^{-2} \text{ year}^{-1} \text{ km}^{-1}$

relative error RE measures the dimensionless ratio of measured and estimated value as $z(x)/z^*(x)$. The Pearson coefficient of correlation R measures the quality of

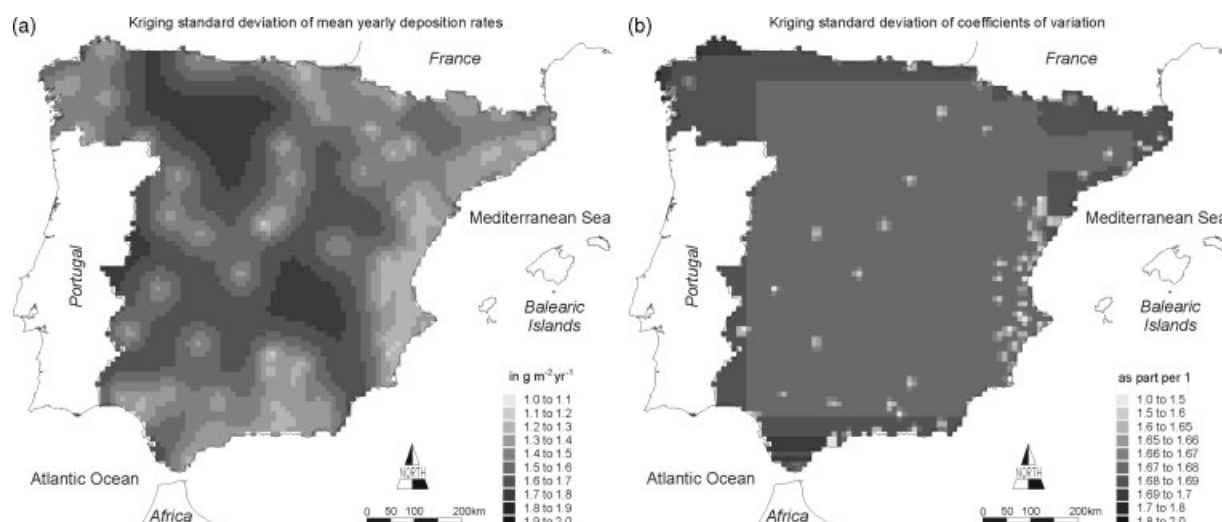


Figure 8. Kriging standard deviation (KSD) of bulk Cl^- deposition rate in continental Spain. (a) KSD of the mean value ($\text{g m}^{-2} \text{ year}^{-1}$). (b) KSD of the coefficient of variation. Values are discretized in cells of $10 \text{ km} \times 10 \text{ km}$

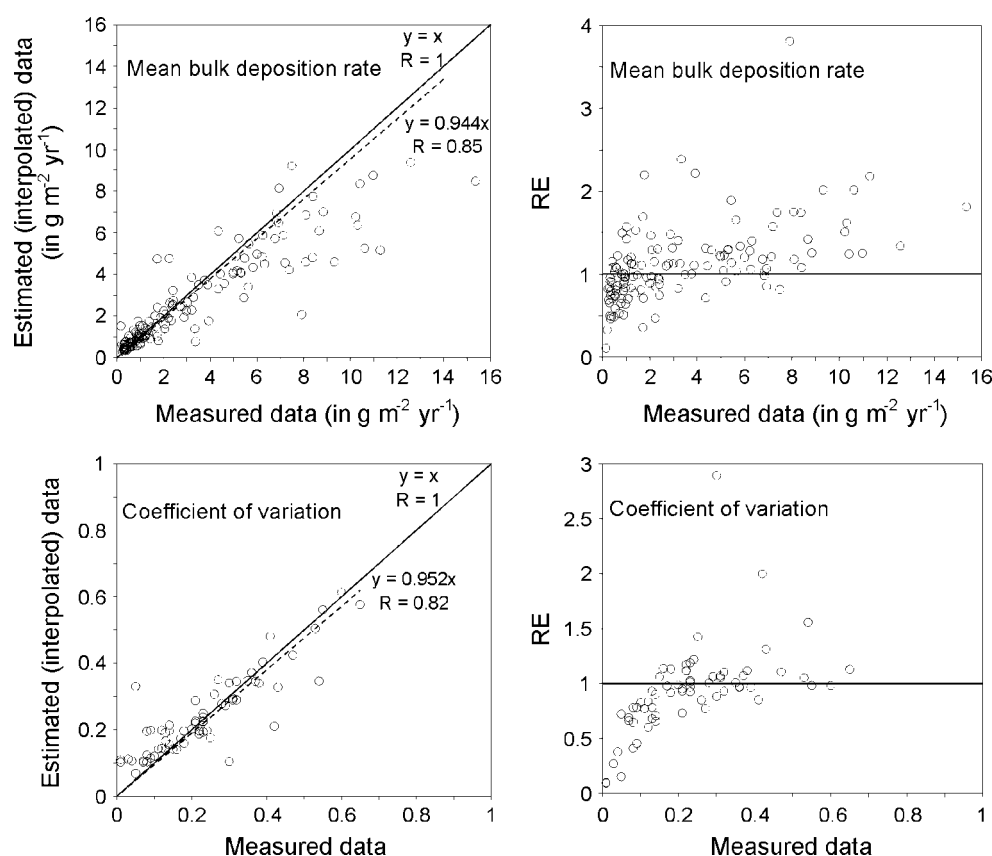


Figure 9. Relative error RE and Pearson's coefficient of correlation R between measured and estimated data by ordinary kriging of mean values and coefficients of variation of bulk Cl^- deposition rate datasets. The comparison is done for the same geographic positions

the linear ratio initially expected between measured and estimated data (Davis, 1986). A good estimate should provide $\text{RE} = 1$ and $R = 1$. RE usually varies from 0.4 to 2 for the set of mean deposition rates and coefficients of variation (Figure 9), with extreme values between 0.1 and 3 respectively. The bias is relatively more important for the lowest values of both variables. RE and R show that the geostatistical estimates produce a slight tendency to decrease the highest values and a certain tendency to increase the lowest measured values.

DISCUSSION

The regional magnitude of bulk Cl^- deposition rate in continental Spain is controlled by the marine origin of salinity associated with air masses and cloud fronts entering from the Atlantic Ocean, and the local effect on the eastern and southeastern areas of wet Mediterranean air masses when they find cold air above. The control that these global meteorological patterns exert on the amount and origin of bulk Cl^- deposition is similar to what is

described in other regions of the northern hemisphere by Eriksson (1960), Richter *et al.* (1983), Li (1992) and Gustafsson and Hallgren (2000).

The ordinary kriging to map spatial distribution of atmospheric bulk Cl^- deposition rate in continental Spain reproduces reasonably the behaviour of the average value data observed in inland and coastal zones, where the variable stabilizes at a finite distance and is slightly discontinuous. Nevertheless, the coefficients of variation dataset shows a poor spatial correlation at the origin and a poorly defined fit to the sill (Figure 5). This results from the large and uncorrelated local heterogeneity, since values from different time periods and generally short monitoring periods are compared. Several workers have previously used this method and similar functions for the same purpose in the USA (National Atmospheric Deposition Program (NADP)/National Trends Network, 2000), southern Sweden (Gustafsson and Hallgren, 2000) and eastern Spain (Carratalá *et al.*, 1998).

The bulk Cl^- deposition rate at sites on the Atlantic coast varies from 1 to 30 $\text{g m}^{-2} \text{ year}^{-1}$, with some anomalies due to sampling gaps at the coastline (Figure 6a). The difference between bulk and wet Cl^- deposition rates varies from 1% to 10%; figures between 4% and 20% were obtained by Gustafsson and Hallgren (2000) for southern Sweden. The northwestern mountain ranges of the Iberian Peninsula act as an effective barrier to the inland movement of air masses carrying marine Cl^- (Figure 6d). This results in the sharp gradient along the north and west coasts that diminishes more or less exponentially toward inland zones, depending on how exposed they are to incoming oceanic fronts. The territorial gradient is $\sim 0.2\text{--}0.3 \text{ g m}^{-2} \text{ year}^{-1} \text{ km}^{-1}$ on the northern coast, $\sim 1\text{--}2 \text{ g m}^{-2} \text{ year}^{-1} \text{ km}^{-1}$ on the northeastern coast and $\sim 0.4 \text{ g m}^{-2} \text{ year}^{-1} \text{ km}^{-1}$ on the southeastern coast (Figure 7), in good agreement with the values proposed by Richter *et al.* (1983) for the southeastern USA.

The western Mediterranean air masses that produce convective rains also carry marine Cl^- from the Mediterranean Sea. Therefore, the predominant influence on Cl^- deposition in eastern and southeastern Spain causes broad Mediterranean-dominated deposition. The bulk Cl^- deposition rate on the Mediterranean coast is between 1 and 15 $\text{g m}^{-2} \text{ year}^{-1}$, with values that may exceed these figures if the sampling is done close to the coast (Figure 6a). Territorial gradients of $\sim 0.1 \text{ g m}^{-2} \text{ year}^{-1} \text{ km}^{-1}$ have been measured on the east coast and $0.8\text{--}4 \text{ g m}^{-2} \text{ year}^{-1} \text{ km}^{-1}$ on the south-east coast of the Iberian Peninsula (Figure 7). The difference between bulk and wet Cl^- deposition on the Mediterranean coast is $\sim 25\%$. The relative abrupt relief that determines the variation in the precipitation volume (Figure 6c) and its chemical content also determines (Figure 6d), along with wind speed and direction, a high dry Cl^- deposition rate along the peninsular southeast coast which can be up to 50% of the bulk Cl^- deposition rate (Figure 6a and d). Similar values and trends have been described in Israel (Eriksson and Khunakasem,

1969), eastern Spain (Carratalá *et al.*, 1998), northeast of Spain (Iglesias *et al.*, 1997) and Corsica (Löye-Pilot and Morelli, 1988).

In the interior of the Iberian Peninsula, the absence of significant orographic barriers favours the movement of air masses and cloud fronts, mainly from the Atlantic Ocean. The bulk Cl^- deposition rate is reasonably homogeneous and varies from 0.2 to 0.6 $\text{g m}^{-2} \text{ year}^{-1}$, whereas the wet Cl^- deposition rate varies from 0.2 to 0.5 $\text{g m}^{-2} \text{ year}^{-1}$. The difference between the two types of deposition is around 10–30% and is associated with a certain recycling of atmospheric dust, mainly in summer, when precipitation is low in Spain. These values are coherent with the figures of around 23% proposed by Eriksson (1960) and Bentley *et al.* (1986) in the continental USA. Very low territorial gradients (on the order of $5 \times 10^{-3} \text{ g m}^{-2} \text{ year}^{-1} \text{ km}^{-1}$, or even lower than $10^{-3} \text{ g m}^{-2} \text{ year}^{-1} \text{ km}^{-1}$) have been measured that are similar to those measured by Wood and Sanford (1995) and Minor *et al.* (2007) in inland zones of the USA.

In some inland zones of the Iberian Peninsula where there are evaporitic rock outcrops and an important wind regime, such as in the Ebre River basin or in the Guadix basin (Granada), bulk Cl^- deposition rates of between 1 and 2 $\text{g m}^{-2} \text{ year}^{-1}$ have been measured. They exceed the usual range of 0.2–0.5 $\text{g m}^{-2} \text{ year}^{-1}$ measured in their geographic surroundings. Terrestrial contribution of Cl^- is associated mainly with dry atmospheric deposition during dry-spell periods (Figure 6d).

In urban and industrial areas, high bulk Cl^- deposition rates have been measured, partly due to anthropogenic contributions of Cl^- . Fuel combustion and burning of plastics and hydrocarbons, among other punctual causes (e.g. coal burning, which produces gaseous HCl ; Alastuey *et al.*, 1999), can contribute between 1 and 30% of the total mean value of the bulk Cl^- deposition rate in Madrid (Hontoria *et al.*, 2003), in Barcelona (Custodio *et al.*, 1985), and in some industrial coastal areas of southern and northeastern Spain (Usero and Gracia, 1986; Feliu *et al.*, 2001). This is also observed in other Spanish cities, such as Sevilla, Bilbao, Cartagena and Valencia (Figure 6a), and is common in other cities around the world (Martens *et al.*, 1973; Löye-Pilot and Morelli, 1988; Li, 1992).

The coefficient of variation of bulk Cl^- deposition rate (Figure 6b) is a function of the time variability of precipitation and its saline content, and the time variability of saline contribution from dry deposition. The variability of precipitation in Spain is known from the study of rain-gauge data for over 100 years (Font, 1983; MIMAM, 2000).

The coefficient of variation values range from 0.1 to 1. A value equal to unity supposes that a mean value of bulk Cl^- deposition equal to X theoretically varies between 0 and $2X$ for 64% of the cases. In this situation, the coefficient of variation is not a good indicator of estimated mean value natural uncertainty because the variable is skewed, and so it is better to consider the

logarithmic transformation of observations. Coefficients of variation between 0.1 and 0.5 can be used as a reasonable indicator of uncertainty, but not higher values.

CONCLUSIONS

When datasets contain sampling periods of less than 5 years, and usually of only 1 year, there is a notable uncertainty in the estimation of mean yearly bulk Cl^- deposition rates due to the short sampling period. This uncertainty is evaluated at around 30% of the value estimated by comparing available data with other data from the Spanish EMEP network stations, which have precipitation records and chemical rainfall data for longer periods.

The mean yearly atmospheric bulk Cl^- deposition rate in the centre of the Iberian Peninsula varies from 0.2 to 0.5 $\text{g m}^{-2} \text{ year}^{-1}$ with territorial gradients around or less than $5 \times 10^{-3} \text{ g m}^{-2} \text{ year}^{-1} \text{ km}^{-1}$, whereas along the Atlantic and Mediterranean coasts it varies from 1 to 30 $\text{g m}^{-2} \text{ year}^{-1}$ and from 1 to 15 $\text{g m}^{-2} \text{ year}^{-1}$ respectively, with a strong gradient diminishing inland of between 0.1 and 1 $\text{g m}^{-2} \text{ year}^{-1} \text{ km}^{-1}$. The coefficient of variation of bulk Cl^- deposition rate decreases from ~0.5 on the northeastern coast to 0.1 in the interior, and increases again from 0.3 in the mountainous relief in the centre of the peninsula to 0.4 or more in the southeast. The kriging standard deviation for the mean values and coefficients of variation is similar to the estimate in coastal zones and is somewhat greater than one order of magnitude in the interior of the peninsula. The spatial estimate of bulk Cl^- deposition rate is somewhat underestimated in coastal zones and somewhat overestimated inland when there is scarce initial data available, in a range that can vary from 0.5 to 2 with respect to initial data in the same geographic domains.

The spatial interpolation of atmospheric bulk Cl^- deposition rate is satisfactory in most of the Spanish peninsular territory, although it is somewhat deficient in zones with highly varied orography and in coastal areas where there is scarce data available and the kriging standard deviation is ~1.9 $\text{g m}^{-2} \text{ year}^{-1}$. The calculation of recharge rate to aquifers by rain in continental Spain using the Cl^- ion balance is rather uncertain along the coast due to the existence of territorial gradients higher than 1 $\text{g m}^{-2} \text{ year}^{-1} \text{ km}^{-1}$ in bulk Cl^- deposition rate, but is potentially better inland, where territorial gradients are lower than $5 \times 10^{-2} \text{ g m}^{-2} \text{ year}^{-1} \text{ km}^{-1}$.

ACKNOWLEDGEMENTS

We would like to thank the endowment of the Spanish Research Project HID1999-0205. We would also like to thank the Geological Survey of Spain (IGME) laboratory and the efforts of many people in several different organizations that have cooperated in sampling and in organizing the initial information. We especially thank the IGME technicians who participated in sampling

bulk deposition at the temporary IGME stations and the technicians at the National Meteorological Institute and the Ministry of the Environment's General Secretariat for Environmental Quality for rainfall data acquired from the Spanish EMEP network stations. The first author is also grateful to the Ministry of Education and Science of Spain for a 'Juan de la Cierva' Programme Contract (reference JCI-2007-334). We also wish to express our gratitude to Dr Xavier Sánchez-Vila (Department of Geotechnical Engineering, Technical University of Catalonia) and three anonymous reviewers for their valuable advice and constructive comments.

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