

Chemical signature of Saharan dust on dry and wet atmospheric deposition in the south-western Mediterranean region

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ABSTRACT

We studied if the presence of Saharan dust intrusions and the rains modify the chemical signature of the wet and dry deposition in the southern Iberian Peninsula. We have sorted the 109 sampling weeks by the presence (rainy weeks) or absence (dry weeks) of rain and by the occurrence or not of Saharan dust intrusions. Dry deposition dominated the delivery of particulate material (PM), total phosphorus (TP), soluble reactive phosphorus (SRP), Ca^{2+} , Mg^{2+} and K^+ , whereas wet deposition dominated the delivery of Na^+ , total nitrogen, NO_3^- and SO_4^- . In the dry weeks, the presence of Saharan dust intrusions lead to higher inputs of PM, TP, SRP, Ca^{2+} , Mg^{2+} and K^+ in the dry deposition. Conversely, in the rainy weeks, there were no differences in mean values of dry deposition irrespective of the occurrence of Saharan dust intrusions. Nevertheless, in the presence of Saharan intrusions and some rain, the weekly collection of PM, TP and Ca^{2+} in dry deposition were significantly higher and increased as rainfall was lower. By contrast, the ions Cl^- and Na^+ in wet deposition were higher in absence of Saharan dust intrusion and increased as rainfall increased.

Keywords: Saharan dust, dry deposition, wet deposition, major ions, rain–dust interactions

1. Introduction

Aerosol deposition has a relevant effect on terrestrial and aquatic ecosystems through the supply of limiting elements (see Chadwick et al., 1999; Jickells et al., 2005). The main source of aerosols in the atmosphere at the global scale is the dust injected from arid regions which dominates aerosol loadings compared to anthropogenic sources (Schlesinger, 1997). The largest and most persistent sources of coarse aerosol (particles of supramicron size) are located in the Northern Hemisphere, mainly in the ‘dust belt’ that extends from the west coast of North Africa, over the Middle East, Central and South Asia, to China (Prospero et al., 2002). Therefore, there are great differences in the content of dust aerosol among world localities depending on their geographical localisation with respect to this ‘dust belt’ (Mladenov et al., 2011).

Aerosol deposition occurs through rain washout (named wetfall or wet deposition), or by direct sedimentation during periods without rain (named dryfall or dry deposition). Some studies on atmospheric deposition have been carried out using ‘bulk’ collectors that mix both dryfall and wetfall, precluding their discrimination and specific characterisation. This fact has been considered of minor importance in rainy areas where dryfall can be neglected compared with wetfall (Loÿe-Pilot and Martin, 1996) or dryfall does not basically modify the chemical signature of the wet deposition (Avila and Alarcón, 1999). However, other studies have underlined the significance of dry deposition that, in some cases, can be the dominant fraction of the total deposition (Lovett, 1994). Dryfall is particularly relevant in arid and semi-arid regions where intense dust loadings take place (Kubilay et al., 2000; Morales-Baquero et al., 2006; Pulido-Villena et al., 2006). In such regions, it is necessary to separately quantify wet and dry deposition to achieve a more comprehensive understanding of the atmospheric deposition and their corresponding chemical signatures under the influence of

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dust loading or in its absence. In this work, we use the term chemical signature of wet deposition as the sum of the chemical composition of rain water plus the soluble fraction of particulate aerosol captured by the rain. The chemical signature of dry deposition is the fraction of particulate aerosols soluble in ultrapure water. In both cases, the elements in these soluble phases have a direct impact on the ecosystem biogeochemistry.

The Iberian Peninsula is exposed to frequent Saharan dust intrusions and presents a strong precipitation gradient, from less than 200 mm of mean annual rain in the south-east to more than 2000 mm in the north-west (MMA, 2000). Previous works carried out in Sierra Nevada (south-east of the Iberian Peninsula) have reported a relative higher contribution of dryfall to total atmospheric deposition of particulate matter (PM), water soluble organic carbon (WSOC), total phosphorus (TP), total nitrogen (TN) and calcium (Morales-Baquero et al., 2006; Pulido-Villena et al., 2006, Mladenov et al., 2008). Other studies in the north-eastern Iberian Peninsula have pointed to the significance of Saharan dust on the chemistry of 'bulk' deposition (Camarero and Catalan, 1993; Avila et al., 1998; Avila and Alarcón 1999; Avila and Peñuelas, 1999). Despite these efforts, the effects of Saharan dust on the chemistry of wet and dry deposition remain scantily explored (Izquierdo et al., 2012).

In this study, we determined the chemical signature of Saharan dust intrusions on wet and dry atmospheric deposition in the south of the Iberian Peninsula. This region is very suitable to explore the significance of Saharan dust on both types of deposition because it has long period without rain and is influenced by frequent Saharan dust intrusions.

2. Material and methods

This study was conducted in Sierra Nevada, a remote mountain site located in the south of the Iberian Peninsula, close to the Mediterranean Sea (<25 km) (Fig. 1). The area is located far from direct human activity and is highly influenced by Saharan dust intrusions which make it an ideal site to study the deposition of long-range transported aerosol (Morales-Baquero et al., 2006; Pulido-Villena et al., 2006). This site is located in a semi-arid region with annual rainfall of ≈ 450 mm.

2.1. Sampling and chemical analyses

Separate samples of dry and wet deposition were collected weekly from December 2000 to December 2002 using a MTX[®] ARS 1010 automatic deposition sampler located at 1000 m asl (36°56'N, 3°30'W). These samplers discriminate between dry and wet atmospheric deposition using a

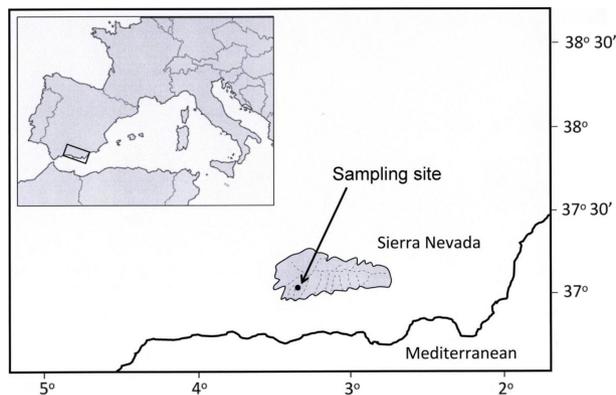


Fig. 1. Location of the study site, in the south-western Mediterranean Region.

humidity sensor that activate an aluminium lid to cover/uncover two (dry and wet) buckets. Every sampling date, dry and wet deposition buckets were replaced and taken to the laboratory. The dry deposition sample was obtained by rinsing the bucket with 1000 mL of Milli-Q[®] ultrapure water and this solution was saved for the chemical analyses. The volume of rain in the wet deposition bucket was recorded, and a 1000-mL aliquot was used for analysis. If rain volume was <1000 mL, it was brought up to that volume with Milli-Q ultrapure water. At the end of the study period, 109 samples were collected. Despite the complexity in the collection of dry atmospheric deposition (Wesely and Hicks, 2000), the comparatively large size of Saharan dust aerosol (supramicrons) (Alados-Arboledas et al., 2003; Mladenov et al., 2010) that are submitted to long-range transport (Prospero, 1996) makes that sedimentation is the main delivery process and likely unaffected by the specific collector properties. Nevertheless, the fluxes of some elements with gaseous compounds as N and S may be underestimated with this procedure. Concentration of PM in dry and wet deposition was determined as dry weight (60°C, 24 h) using Whatman GF/F glass fibre filters. Prior to filtration, 50-mL subsamples were taken to analyse TP and TN concentration. The filtrate was used for analysing soluble reactive phosphorus (SRP), nitrate (NO_3^- -N), sulphate (SO_4^{2-} -S), silicate (SiO_2 -Si), chloride (Cl^-), and calcium (Ca^{2+}), potassium (K^+), sodium (Na^+) and magnesium (Mg^{2+}). Data on PM, TP, TN, SRP and Ca^{2+} have been published elsewhere to assess their effects on alpine lake chemistry and biology (Morales-Baquero et al., 2006; Pulido-Villena et al., 2006; Pulido-Villena et al., 2008a). These values were incorporated in the data pool under the different approach of this work. NO_3^- was analysed following the ultraviolet spectrophotometric method (APHA, 1992); SO_4^{2-} and Cl^- analyses were performed with a Dionex[®] DX100 ionic chromatographer and Ca^{2+} , Na^+ , K^+ and Mg^{2+} were

determined by atomic absorption with a Perkin Elmer® 5100 spectrometer.

The concentration of all chemical species measured in dry and wet deposition samples, collected during each week, was converted to units of daily deposition by considering the sampler area (0.07 m²) and the rain volume (only for wet deposition). This approach for the determination of atmospheric deposition implies that the term ‘dry deposition’ for SRP, NO₃⁻, SO₄²⁻, SiO₂, Cl⁻, Ca²⁺, K⁺, Na⁺ and Mg²⁺ designates the fraction contained in dry deposition that is soluble in ultrapure water. Hereafter, the following terms will be used to refer to the different forms of atmospheric deposition: dry deposition (soluble fraction for anions and/or in suspension for TP, TN and PM), wet deposition (chemical species dissolved in rainwater and/or in suspension for TP, TN and PM), and total deposition (sum of dry and wet deposition).

2.2. Statistical analysis

To investigate the influence of Saharan dust intrusions on the amount and chemical composition of dry and wet atmospheric deposition we compared mean values between the weeks sorted depending on the presence or not of rain and Saharan dust intrusions (Table 1). Saharan dust intrusions over the Iberian Peninsula during the study period were identified after Querol et al. (2002, 2003). These authors developed the methodology for the alert network for Saharan intrusion over the Iberian Peninsula based on: (1) measurements of total particles in suspension; (2) backward trajectories analyses; (3) TOMS (Total Ozone Mapping Spectrometer) aerosol index analyses; (4) Image analysis from SeaWiFS satellite (Goddard Space Flight Centre, NASA); and (5) Saharan dust distribution according to SKIRON and DREAM-ICOD models. Comparisons between means were performed using *t*-tests when it was possible and with the non-parametric Kolmogorov–Smirnov test to avoid violation of assumptions regarding distribution of measures. The analysis of covariance (ANCOVA) combines one-way analysis of variance with linear regression. This analysis allows comparing one categorical variable in two groups taking into account the

Table 1. Number of weeks with absence of rain (dry weeks) and with presence of rain (rainy weeks), affected or not by Saharan dust intrusions, during the 2-year study period

	No intrusion	Intrusion	Total
Dry weeks	23	31	54
Rainy weeks	24	25	49
Total	47	56	103

variability of another continuous variable, called covariate. The ANCOVA’s were used to assess the effect of both Saharan dust events and the rain. Saharan dust events were the categorical variable (presence or absence in the week) and the weekly rain was the covariate (amount of rain during the week). Statistical analyses were performed using Statistica Software (StatSoft Inc., 1997).

3. Results and discussion

3.1. Total deposition

The mean annual precipitation was 503.7 mm (Table 2), with maximum rainfall of 189 mm in November 2002 and several consecutive weeks without rain (5 and 11 weeks in 2001 and 2002, respectively). PM total deposition (mean annual value 11.1 g m⁻²) fitted the regional trend of dust deposition reported for the Mediterranean region with values declining with distance from the north of Africa and toward the west (Goudie and Middleton, 2001). Total deposition of TP and Ca²⁺ also fitted the above mentioned regional distribution pattern. Total TN deposition was lower than reported for central Europe and the eastern part of Mediterranean. More seasonal details about PM, TP, TN and Ca²⁺ deposition can be found in Morales-Baquero et al. (2006) and Pulido-Villena et al. (2006).

Mean total deposition of NO₃⁻ was in the lower range recently found in the Mediterranean region while SRP deposition was similar to other Mediterranean areas (Table 2). Total deposition of SO₄²⁻ was lower than in northern Italy, and in the eastern Mediterranean area (Table 2). The deposition of silicate was lower than the values reported for the north-western Mediterranean region (Bartoli et al., 2005) and much lower than that found by Anderson and Downing (2006) in an agricultural area. However, the scarcity of data on silicate deposition in the literature makes this comparison premature. Total deposition of Na⁺, Mg²⁺, Cl⁻ and K⁺ was lower than the high values reported for the eastern Mediterranean in a location close to the sea (Al-Momani et al., 1995). It is interesting to note that while the total deposition of Na⁺ and Mg²⁺ in this study was similar to the reported values for northern Italy, the total deposition of Cl⁻ and K⁺ was lower (Table 2). The low values of total deposition of Cl⁻ compared to Na⁺ and Mg²⁺ would indicate a deficit of Cl⁻ with respect to sea salt. Moreover, the low deposition of Cl⁻ and K⁺ observed in this study also suggests a scarce influence during the study period of biomass burning, which is a major source of these chemical species in the atmospheric deposition (Li et al., 2003).

Table 2. Daily mean values and range ($\text{m}^{-2} \text{d}^{-1}$) of dry, wet and total deposition from December 2000 to December 2002

ratio	Dry deposition		Wet deposition		Dry/wet	Total deposition		Some reported values of total deposition
	<i>n</i>	Mean (min–max)	<i>n</i>	Mean (min–max)		<i>n</i>	Mean (min–max)	
PM, mg	108	23.6 (0.3–105.8)	109	6.8 (0.0–95.8)	3.49	108	30.4 (0.83–132.2)	34.2 ¹
TP, μmol	108	1.0 (0.03–3.1)	108	0.6 (0.0–9.7)	1.81	107	1.6 (0.1–10.8)	3.5 ¹
SRP, μmol	109	0.4 (0.0–2.1)	104	0.1 (0.0–1.0)	3.5	104	0.5 (0.0–2.4)	0.05–5.3 ² ; 0.27–0.36 ³
TN, μmol	105	49.3 (6.6–306.3)	107	64.0 (0.0–517.2)	0.78	103	115.2 (17.2–533.8)	–
NO_3^- -N, μmol	107	10.2 (0.4–43.7)	108	18.2 (0.0–128.8)	0.56	106	28.8 (0.4–134.5)	49.6–130.7 ⁴
SiO_2 -Si, μmol	106	2.34 (0.39–8.08)	106	2.2 (0.0–28.4)	1.04	104	4.7 (0.7–31.8)	31 ⁵ ; 59.6 ⁶
Ca^{2+} , μmol	107	68.5 (13.4–169.2)	107	44.1 (0.0–440.9)	1.55	105	114.0 (13.9–559.8)	67.9 ⁷
nss Ca^{2+} , μmol	107	66.8 (12.6–167.1)	107	42.6 (0.0–438.6)	1.57	105	110.8 (13.2–556.2)	–
Na^+ , μmol	105	58.2 (21.4–432.1)	108	67.1 (0.0–704.8)	0.87	106	123.4 (21.4–770.9)	146.3–175.1 ⁸ ; 1309.6 ⁹
Mg^{2+} , μmol	107	10.1 (0.8–94.6)	108	8.0 (0.0–56.2)	1.26	106	18.1 (0.8–94.6)	11.2–15.9 ⁸ ; 156.2 ⁹
nss Mg^{2+} , μmol	107	4.7 (0.00–90.6)	108	2.4 (0.0–43.3)	1.91	106	6.9 (0.0–90.6)	–
K^+ , μmol	107	13.1 (2.2–124.7)	108	8.1 (0.0–362.8)	1.62	106	20.9 (2.6–381.4)	40.8 to 62.5 ⁸ ; 35.6 ⁹
nss K^+ , μmol	107	11.7 (0.0–123.9)	108	6.8 (0.0–358.7)	1.70	106	18.2 (0.0–376.4)	–
Cl^- , μmol	106	27.4 (2.4–300.0)	108	29.3 (0.0–533.3)	0.93	105	57.5 (3.6–597.3)	152.9 to 194.8 ⁸ ; 1079.5 ⁹
SO_4^{2-} -S, μmol	102	8.8 (1.4–74.6)	104	11.0 (0.00–87.5)	0.80	99	19.9 (1.6–110.7)	30.1 to 36.2 ⁸
nss SO_4^{2-} -S, μmol	102	6.0 (0.00–70.1)	103	7.8 (0.0–83.0)	0.77	99	13.8 (0.0–106.7)	54.8 ⁹
Rain, mm		–	109	1.4 (0.0–16.3)		109	1.4 (0.0–16.3)	

The dry/wet ratio was obtained using the mean values, *n*: number of samples. Note that *n* can be greater than total weeks in Table 1 because we included the first six sampling weeks for which there were no available data on Saharan intrusions.

¹Corsica (Bergametti et al., 1992); ²western Mediterranean (Pulido-Villena et al., 2008b); ³north-eastern Iberian (Izquierdo et al., 2012); ⁴($\text{NO}_3^- + \text{NH}_4^+$) Mediterranean (Markaki et al., 2010); ⁵Mean value of the data reported by Bartoli et al. (2005) for days with rain in north-western Mediterranean; ⁶Agricultural area (USA) (Anderson and Downing, 2006); ⁷north-eastern Iberian Peninsula (Avila et al., 1998); ⁸northern Italy (Pieri et al., 2010); ⁹eastern Mediterranean (Al-Momani et al., 1995).

3.2. Marine ionic ratios and the Cl^- deficit

Dry and wet deposition showed similar ionic ratios with respect to Na^+ (Fig. 2). Non-sea-salt (nss) Ca^{2+} , nss K^+ and nss SO_4^{2-} appeared enriched with respect to the marine proportion of Na^+ , indicating a continental origin (Fig. 2). The proportion of nss Mg^{2+} with respect to Na^+ was in the range of the marine ratio, although there were not correlations between nss Mg^{2+} and Na^+ , neither in dry ($r=0.07$; $p=0.605$) nor wet ($r=0.11$; $p=0.565$) deposition. In contrast, the Cl^- to Na^+ ratio was markedly lower than in marine waters (Fig. 2) indicating a Cl^- deficit.

This deficit of Cl^- in the atmospheric deposition has been previously reported in other studies of the Mediterranean basin. Mihajlidi-Zelic et al. (2006) found a deficit of Cl^- in bulk deposition of a coastal site in the Adriatic Sea with the highest values of Na^+/Cl^- ratios during the driest months. Mihalopoulos et al. (1997) and Koçak et al. (2004) also found Cl^- deficits in lower tropospheric aerosols in the eastern Mediterranean. During the winter, the Na^+/Cl^- ratio reflected the marine ratio whereas during the summer (when the rainfall reaches its lowest values) this ratio increased above the marine ratio. On the other hand, Balestrini et al., (2000) did not find departures of Na^+/Cl^- marine ratio in dry nor wet deposition in five sites of the northern Italy region where the precipitation values

ranged from 852 $\text{mm}\cdot\text{y}^{-1}$ to 1959 $\text{mm}\cdot\text{y}^{-1}$. These precipitation values were markedly higher than the values in this study. All these previous studies suggest a link between dryness and the Cl^- deficit.

Sodium chloride from sea salt can react in the atmosphere with gaseous nitric acid producing sodium nitrate and chloride acid. This reaction can occur in the surface of aerosol particles (Pakkanen, 1996) and a certain fraction of sea-salt Cl^- can be replaced by NO_3^- . In addition, the amount of NO_3^- in sea water is negligible compared with the main ionic concentrations. Therefore, the marine Na^+/Cl^- equivalent ratio of 0.85 can be assumed as representative of the original $\text{Na}^+/(\text{NO}_3^- + \text{Cl}^-)$ ratio in sea water (Pakkanen, 1996). Deviations from 0.85 indicate enrichments or impoverishments of these ions with respect to the marine proportion. Figure 3 shows the mean values of Na^+/Cl^- and $\text{Na}^+/(\text{NO}_3^- + \text{Cl}^-)$ ratios in both dry and wet deposition. The Na^+/Cl^- ratio was above the marine ratio, without statistical differences between dry and wet deposition (Fig. 3A). However, the $\text{Na}^+/(\text{NO}_3^- + \text{Cl}^-)$ ratio decreases markedly in both types of deposition, being close to the marine ratio in the wet deposition and significantly higher in dry deposition (Fig. 3B).

These significant differences between dry and wet deposition in the $\text{Na}^+/(\text{NO}_3^- + \text{Cl}^-)$ ratios, provide some insights in the process of Cl^- losses from the particulate aerosol.

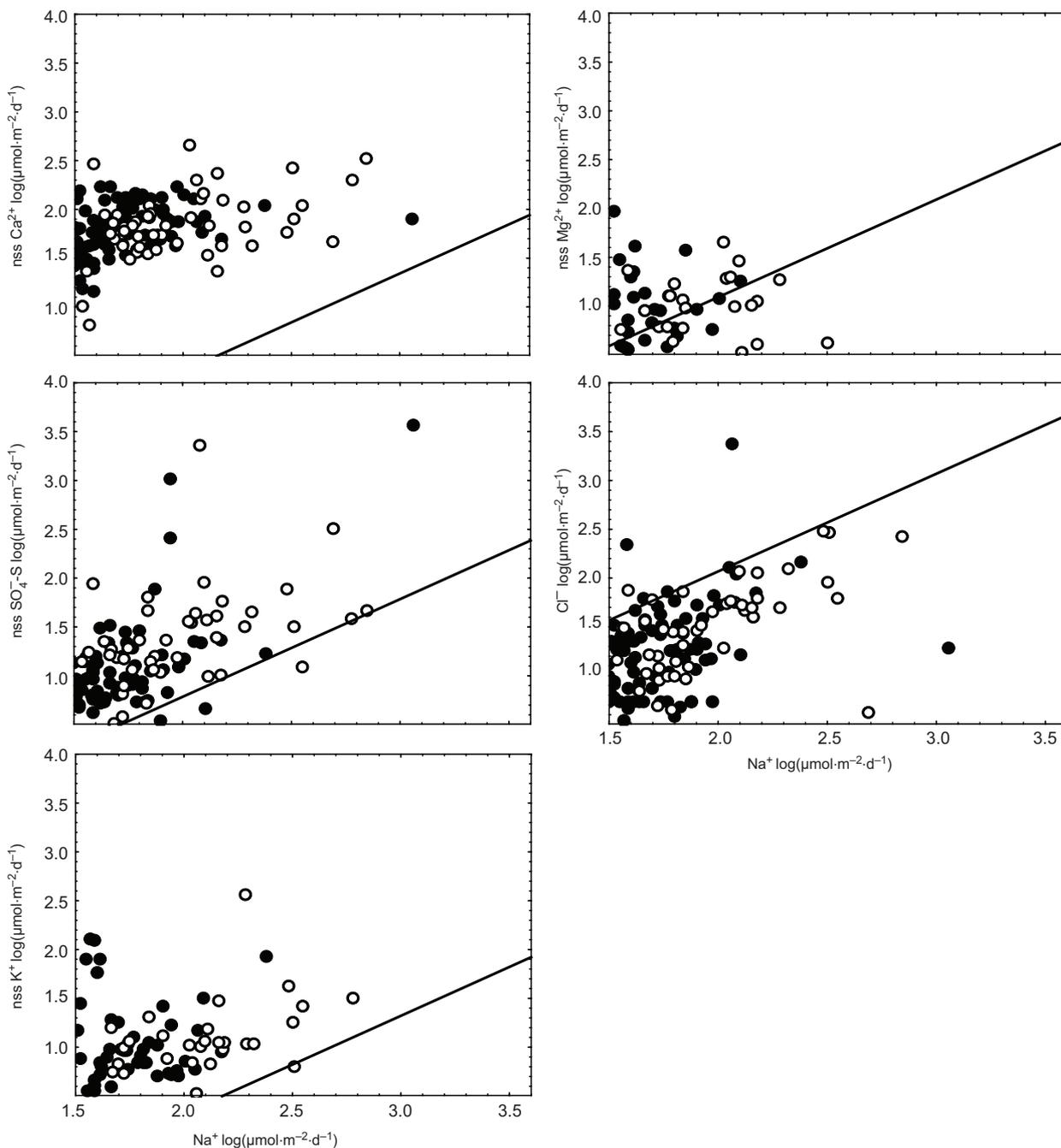


Fig. 2. Non-sea-salt (nss) Ca^{2+} , SO_4^{2-} , K^+ , Mg^{2+} and Cl^- in dry (solid dots) and wet (empty dots) deposition as function of Na^+ . The solid line represents the ratio of these ions to Na^+ in sea water.

The ratio values in wet deposition of about 0.85, or slightly lower, could be attributed to a substitution of Cl^- by NO_3^- in the surface of sea salt or soil particles after reacting with nitric acid. In dry deposition samples, although the ratio $\text{Na}^+ / (\text{NO}_3^- + \text{Cl}^-)$ decreased notably with respect to $\text{Na}^+ / \text{Cl}^-$ ratio, it was higher than the marine proportion, suggesting a loss of Cl^- which it is not exchanged by

NO_3^- . Cl^- ions can also evaporate directly (Pakkanen, 1996) or react with other acidic species. Our results suggest a lack of NO_3^- available in dry deposition to substitute Cl^- in the atmospheric particles. In fact, NO_3^- deposition in the south-east of the Iberian Peninsula is scarce compared with other sites from the north of Europe or eastern Mediterranean area and is mostly related to the wet

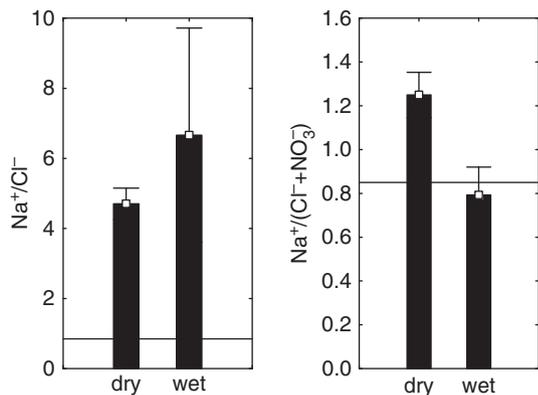


Fig. 3. Mean ratios (bars) and standard errors (whiskers) of: (A) Na^+ to Cl^- in dry and wet deposition (not statistically different; t -test = 0.887; $p = 0.376$) and (B) Na^+ to $(\text{Cl}^- + \text{NO}_3^-)$. These ratios in dry deposition are significantly higher than in wet deposition (t -test = 2.673; $p < 0.01$). Note the change of scale in the two plots. The solid lines represent the Na^+ to Cl^- ratio of 0.85 in sea water.

deposition (Table 2). This process in the study area should be different to what is occurring in the eastern Mediterranean where evidences linking dust and sea salts with nitrates have been previously reported (Mara et al., 2009).

3.3. Dry and wet deposition

Marked differences were observed concerning the relative contribution of dry and wet deposition to total inputs for the different chemical species studied. Dry deposition was the main pathway for the atmospheric delivery of PM, TP, SRP, Ca^{2+} , Mg^{2+} and K^+ , whereas Na^+ , TN, NO_3^- and SO_4^{2-} showed a clear predominance in wet deposition (Table 2).

PM was three times higher in dry than in wet deposition (Table 2). This could be due to the high number of weeks without rain, and the proximity of the study site to Sahara desert. It has been reported that the ratio of dry to wet deposition of dust decreases with the distance from the source of emissions, as the readily dry-deposited substances are depleted from the air mass as they travel downwind (Lovett, 1994).

Concerning phosphorus compounds, TP deposition was almost twice higher in dry than in wet mode, and SRP was more than three times. These results are similar to previous studies showing the predominance of dry over wet deposition for phosphorus (Anderson and Downing, 2006). Phosphorus delivered by deposition is derived mostly from soil and is not incorporated in a great extent into rainfall. The deposition of Ca^{2+} , Mg^{2+} and K^+ were also higher in dry than in wet deposition, but less markedly than for PM, TP and SRP.

The predominance of Na^+ , TN, NO_3^- and SO_4^{2-} in wet deposition indicates that, despite nitrates and sulphates undergoing long-range transport associated with dust (Dentener et al., 1996), the free gaseous phases of these compounds are predominately incorporated into wet deposition. Nevertheless, regarding TN, these results should be considered with precaution because NH_x compounds that can be a significant source of N in dry deposition appear to not be properly sampled in the dry collectors (Anderson and Downing, 2006).

3.4. Effects of Saharan dust intrusions on the chemistry of dry and wet deposition

In the dry weeks (complete absence of rain), the effect of the Saharan dust intrusion is evidenced by the statistically significant increase of most chemical species deposited (Table 3). Only dry deposition of SiO_2 , NO_3^- , SO_4^{2-} and Na^+ did not show significant increases linked to the occurrence of Saharan dust events.

In the rainy weeks, the effect of Saharan dust intrusions on dry deposition was not statistically significant for any of the chemical species analysed (Table 3). This absence of statistical significance can be interpreted as the effect of the atmospheric washout by the rain that reduces the availability of aerosols for the following dryfall. For instance, the total (dry+wet) PM deposition in weeks submitted to Saharan dust intrusions was similar in rainy weeks ($19.5 + 15.6 \text{ mg m}^{-2} \text{ d}^{-1}$ [wet+dry, respectively]) to that in dry weeks ($36.7 \text{ mg m}^{-2} \text{ d}^{-1}$, dry deposition). Similarly, the total PM deposition in weeks without Saharan dust intrusions was similar in rainy weeks ($12.1 + 15.5 \text{ mg m}^{-2} \text{ d}^{-1}$ [wet+dry, respectively]) and in dry weeks ($22.5 \text{ mg m}^{-2} \text{ d}^{-1}$, dry deposition) (Table 3). Therefore, these results point out that the total PM deposition was similar irrespectively of the occurrence of rain, and that the effect of rain washout only leaves less PM (and associated soluble ions) for the following dry deposition. On the other hand, there are no effects of Saharan dust on wet deposition except the marginally significant lower quantities of Na^+ collected (Table 3).

The comparison of the chemical species between dry and wet deposition showed important differences in weeks with rain events. There were higher deposition rates of TN, NO_3^- , Na^+ and SO_4^{2-} in wet than in dry mode and particularly higher for TN, Cl^- , SO_4^{2-} and Na^+ in weeks without Saharan dust intrusions (Table 3). Since TN, Cl^- , SO_4^{2-} and Na^+ have either a gaseous phase or a marine origin, it is highly probable that an important source of these last elements is sea salt or gases captured by the westerly winds from the Atlantic Ocean, which are the main drivers of rain in the study area (Naya, 1984).

Table 3. Mean quantities (\pm standard error) of the chemical species collected in dry weeks (complete absence of rain) and in rainy weeks (presence of rain) from December 2000 to December 2002. p shows probability values according to Kolmogorov–Smirnov test for mean differences

	Dry weeks			Rainy weeks					
	Dry deposition			Dry deposition			Wet deposition		
	Saharan intrusions	No intrusions	p	Saharan intrusions	No intrusions	p	Saharan intrusions	No intrusions	p
PM	36.7 ± 26.2	22.5 ± 15.6	< 0.025	19.5 ± 19.5	15.5 ± 12.5	> 0.1	15.6 ± 21.5	12.1 ± 16.2	> 0.1
TP	1.4 ± 0.7	1.0 ± 0.9	< 0.005	1.0 ± 0.6	0.7 ± 0.6	> 0.1	0.8 ± 0.6	1.5 ± 2.2	> 0.1
SRP	0.5 ± 0.4	0.4 ± 0.5	< 0.1	0.3 ± 0.4	0.3 ± 0.3	> 0.1	0.2 ± 0.2	0.2 ± 0.3	> 0.1
TN	50.5 ± 25.3	38.3 ± 20.1	< 0.005	64.9 ± 77.7	48.2 ± 54.1	> 0.1	117.2 ± 108.4	146.6 ± 124.6	> 0.1
NO₃⁻-N	13.3 ± 10.3	8.8 ± 6.0	> 0.1	10.2 ± 10.3	8.3 ± 7.4	> 0.1	36.0 ± 26.9	40.0 ± 33.4	> 0.1
SiO₂-Si	2.8 ± 1.8	2.4 ± 1.7	> 0.1	2.0 ± 1.2	1.9 ± 1.3	> 0.1	3.9 ± 4.0	5.5 ± 6.4	> 0.1
Ca²⁺	96.7 ± 42.9	55.6 ± 27.6	< 0.025	67.3 ± 33.0	52.2 ± 30.3	> 0.1	98.4 ± 101.3	76.0 ± 51.1	> 0.1
nss Ca²⁺	95.5 ± 42.7	54.6 ± 27.5	< 0.025	66.1 ± 32.7	50.7 ± 30.1	> 0.1	96.6 ± 100.7	72.6 ± 49.7	> 0.1
Na⁺	52.9 ± 23.8	45.6 ± 22.8	> 0.1	58.7 ± 46.1	69.9 ± 84.1	> 0.1	83.4 ± 64.4	153.4 ± 135.0	< 0.1
Mg²⁺	15.5 ± 17.9	7.0 ± 6.5	< 0.01	10.5 ± 10.0	7.3 ± 5.6	> 0.1	15.7 ± 14.2	17.6 ± 15.6	> 0.1
nss Mg²⁺	9.3 ± 18.4	2.6 ± 6.3	< 0.025	4.4 ± 8.0	2.5 ± 4.6	> 0.1	6.2 ± 9.9	4.7 ± 7.5	> 0.1
K⁺	16.9 ± 30.8	13.8 ± 29.1	< 0.1	13.0 ± 21.5	9.2 ± 12.1	> 0.1	22.2 ± 71.4	12.5 ± 12.5	> 0.1
nss K⁺	15.8 ± 31.0	12.8 ± 29.1	< 0.05	11.8 ± 20.9	7.8 ± 11.8	> 0.1	20.4 ± 70.8	9.3 ± 10.3	> 0.1
Cl⁻	36.0 ± 42.0	17.4 ± 16.2	< 0.01	27.4 ± 36.7	27.9 ± 59.4	> 0.1	28.6 ± 24.1	87.2 ± 124.6	> 0.1
SO₄²⁻-S	10.2 ± 8.9	9.4 ± 15.0	> 0.1	9.5 ± 13.1	5.7 ± 5.6	> 0.1	18.5 ± 18.4	28.7 ± 24.2	> 0.1
nss SO₄²⁻-S	7.2 ± 8.5	7.0 ± 14.4	> 0.1	6.5 ± 13.0	3.0 ± 4.5	> 0.1	14.7 ± 18.1	21.2 ± 22.5	> 0.1

Dry deposition can be collected in both types of weeks and under the influence of Saharan dust intrusion or not. Wet deposition can be collected only in rainy weeks but with or without Saharan dust intrusions. Significant ($p < 0.05$) and marginally significant ($p < 0.1$) differences, are in bold. Units are $\mu\text{mol m}^{-2} \text{d}^{-1}$ except PM in $\text{mg m}^{-2} \text{d}^{-1}$.

Because Saharan dust intrusions and rain events can interact affecting the chemical signature of dry and wet deposition, we performed ANCOVA analyses to test the effect of Saharan dust intrusions (categorical variable, presence vs. absence) on the weekly deposition considering the amount of rain (continuous variable) as a covariate (Table 4). In dry deposition, both Saharan dust intrusions and rain affected the deposition of TP, Ca²⁺ and, marginally, PM. Saharan dust intrusions increased the deposition of these analytes while the amount of rain showed inverse relationships (the higher rain, the lower the analyte quantity) (Fig. 4). Deposition rates of SRP and SiO₂ did not appear to be affected by Saharan dust intrusions although the increases of rain decreased their dry deposition (Table 4). Other chemical species in dry deposition such as TN and Mg²⁺ appeared to be affected by Saharan dust intrusions but not by the quantity of rain. In contrast, dry deposition of NO₃⁻, Na⁺, K⁺, Cl⁻ and SO₄²⁻ did not appear to be affected by dust intrusions nor by the rain quantity (Table 4). These last ions may be linked to atmospheric particles that are removed less efficiently by the type of rain that occurs in the study area. It is known that the size of raindrops and the intensity and duration of the rain events affect the size of particles that are washout from the atmosphere (Praneshia and Kamra, 1997). On the other hand, the below-cloud

scavenging may not be the dominant process in the removal of atmospheric components (Celle-Jeanton et al., 2009).

In wet deposition, only Na⁺ and, marginally, Cl⁻ were influenced by both Saharan dust intrusions and the rain quantity. Saharan dust intrusions decreased the deposition of Na⁺ and Cl⁻, while the quantity of rain increased their deposition (Fig. 5). This result corroborated the marine origin of both ions. The rest of ions and the PM did not appear to be influenced by Saharan dust intrusions in wet deposition (Table 4). In contrast, the quantity of rain affected positively all ions and particles, except nss Mg²⁺ and nss SO₄²⁻. Although it is known that increases in rain reduce the solutes concentration in the wet deposition by dilution (Balestrini et al., 2000), they can still result in higher deposition (Anderson and Downing, 2006) due to larger total washout of the atmosphere as it appears to be the case in this study.

Therefore, the interaction between Saharan dust intrusions and the rain quantity showed two contrasting effects depending on the type (wet or dry) of deposition. Dry deposition of PM, TP and Ca²⁺ were higher in weeks with Saharan dust intrusions and lower quantity of rain, while Na⁺ and Cl⁻ were more representative in wet deposition in weeks without Saharan intrusions and higher quantity of rain.

Table 4. ANCOVA analyses of Saharan intrusions effect (categorical variable) on deposition, taking into account the amount of rain as a covariate (continuous variable). p shows the probability values of F statistic

Source of variation	Dry deposition		Wet deposition	
	F statistic	p	F statistic	p
PM				
Rain	14.31	0.000265	6.04	0.01779
Saharan intrusion	3.49	0.064739	0.25	0.61692
TP				
Rain	6.83	0.01034	6.61	0.01351
Saharan intrusion	7.95	0.00581	0.52	0.47662
SRP				
Rain	4.03	0.04730	12.41	0.00106
Saharan intrusion	0.69	0.40740	0.02	0.88061
TN				
Rain	0.126	0.72320	5.84	0.01988
Saharan intrusion	4.88	0.02953	0.02	0.89492
NO₃⁻-N				
Rain	1.97	0.16366	18.54	0.00009
Saharan intrusion	0.63	0.42902	0.67	0.41732
SiO₂				
Rain	4.00	0.04823	11.56	0.00145
Saharan intrusion	0.80	0.37471	0.02	0.87851
nss Ca²⁺				
Rain	5.52	0.02079	8.08	0.00676
Saharan intrusion	16.26	0.00011	1.22	0.27456
Na⁺				
Rain	0.91	0.34354	41.31	0.00000
Saharan intrusion	0.24	0.62715	4.97	0.03082
nss Mg²⁺				
Rain	0.04	0.84646	1.32	0.25663
Saharan intrusion	7.72	0.00656	0.63	0.43111
nss K⁺				
Rain	0.69	0.40861	19.86	0.00006
Saharan intrusion	0.53	0.46818	0.25	0.61606
Cl⁻				
Rain	0.07	0.79635	12.40	0.00105
Saharan intrusion	0.94	0.33539	3.45	0.07037
nss SO₄²⁻-S				
Rain	2.12	0.14891	2.52	0.11988
Saharan intrusion	1.54	0.21748	0.14	0.70759

Significant ($p < 0.05$) and marginally significant ($p < 0.1$) values are in bold.

In a seasonal basis, it is known that Saharan intrusions over Europe increased during spring and summer (Moulin et al. 1997), when the intense heating of Sahara and the consequent development of the North African thermal low originating a convective system that pumps dust up to 5000 m asl (Escudero et al., 2005). These authors also show that a wide majority of these episodes occurs without local convective rains over Iberian Peninsula. Accordingly,

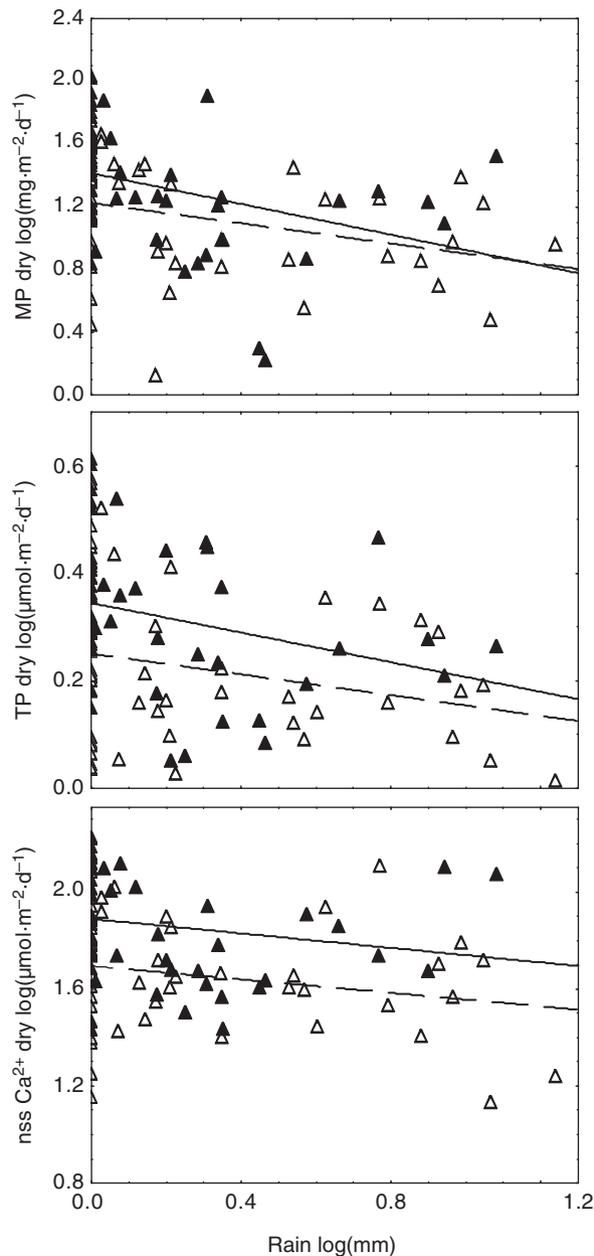


Fig. 4. Particulate matter (PM), total phosphorus (TP) and Ca²⁺ in dry deposition as a function of the rainfall and the presence (solid dots and continuous line) or not (empty dots and dashed line) of Saharan dust intrusions. All relationships are statistically significant according to ANCOVA results shown in Table 4.

satellite measures of aerosol concentration over study area showed its highest values in spring and summer, just when rain shows its lowest values (Fig. 6). The aerosol deposition of PM, TP and Ca²⁺ also follows this seasonal pattern as it was previously reported (Morales-Baquero et al., 2006, Pulido-Villena et al., 2006).

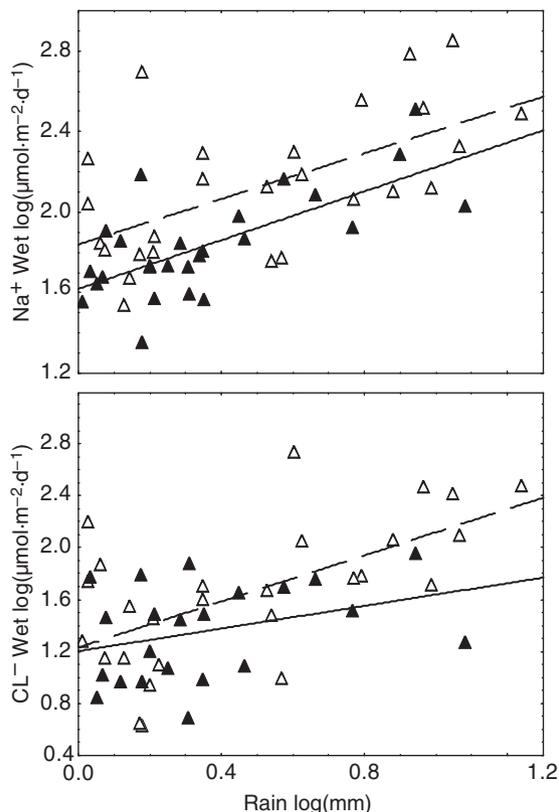


Fig. 5. Na^+ and Cl^- in wet deposition as a function of the rainfall and the presence (solid dots and continuous line) or not (empty dots and dashed line) of Saharan dust intrusions. Na^+ and Cl^- relationships are statistically significant according to ANCOVA results shown in Table 4.

4. Summary and conclusions

Three major conclusions can be extracted from this study. First, dry deposition dominates the atmospheric delivery of PM, TP, SRP, Ca^{2+} , Mg^{2+} and K^+ , while wet deposition dominates the atmospheric delivery of Na^+ , TN, NO_3^- and SO_4^{2-} in the study area; second, the chemical composition of the dry deposition clearly reflected the effect of Saharan dust intrusions during the dry weeks, when the deposition rates of PM, TP, SRP, Ca^{2+} , Mg^{2+} and K^+ were higher than in weeks without intrusions; and third, the wet deposition of ions Cl^- and Na^+ was lower under the influence of Saharan dust intrusions and increased as the quantity of rain increased.

In general, this study underlines the need to quantify dry deposition, particularly in arid and semi-arid regions, which is relevant not just for the amount of soluble substances but also for the chemical species deposited in comparison with the wet deposition. Dry deposition of some elements of biogeochemical interest for ecosystems

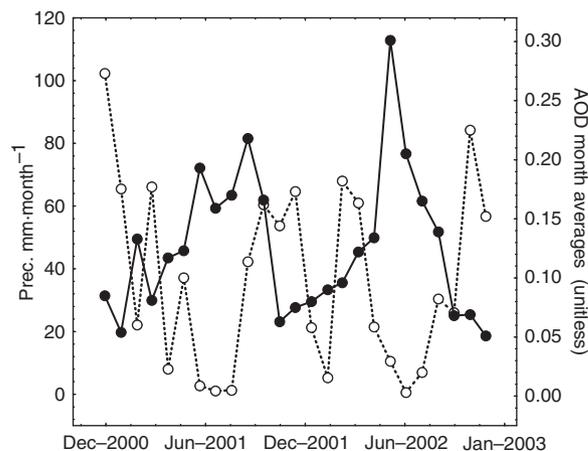


Fig. 6. Time series monthly averages of aerosol optical depth (AOD, solid line) provided by NASA Giovanni portal: (http://gdata1.sci.gsfc.nasa.gov/daac-bin/G3/gui.cgi?instance_id=MISR_Monthly_L3) and precipitation (dashed line): (http://gdata1.sci.gsfc.nasa.gov/daac-bin/G3/gui.cgi?instance_id=GPCC_Monthly). Values are integrated for the study area as shown in the frame of Fig. 1.

(as P, Ca^{2+} , Mg^{2+} and K^+) are therefore related to dust long-range transport. This evidence complements previous studies performed in regions with higher rainfall. For instance, Balestrini et al. (2000) concluded that, in northern Italy, wet deposition reflects long-range transport phenomena, while dry deposition is more linked to local pollution levels. There, the rainfall ($852\text{--}1959\text{ mm}\cdot\text{y}^{-1}$ and absence of months without rain) was much higher than in our locality ($507\text{ mm}\cdot\text{y}^{-1}$ and months without rain). Therefore, the relative contribution of dry and wet deposition for the supply of elements from the atmosphere is, to some extent, depending on the precipitation regime in the area. The dryfall predominance is likely also to be relevant in many other world arid areas, particularly in those ones included within the 'dust belt' zone (Prospero et al., 2002; Mladenov et al., 2011). In these zones, the atmospheric delivery of elements of biogeochemical interest might be both quantitatively and qualitatively different to areas with predominant wet deposition.

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