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Comparison of collection methods to determine atmospheric deposition in a rural Mediterranean site (NE Spain)

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Abstract

Wet-only, dry-only, bulk deposition and deposition of sedimentary particles and gases deposited after the last rain (DAR) were collected weekly at La Castanya station in the Montseny mountains (NE Spain, 41º46'N, 2º21'E) from February 2009 to July 2010. These samples were analysed for pH, alkalinity, and the concentrations of major ions (Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, Ca^{2+}, Mg^{2+}, NH_4^+). Significant differences were observed between bulk and wet-only precipitation, with an enrichment of ions associated to coarse particles in bulk deposition. The comparison between wet and dry fluxes revealed that the removal of compounds at Montseny occurred mainly by wet deposition, which accounted for 74% of total deposition. The dry flux was characterised by the predominance of K^+, Ca^{2+} and Mg^{2+}, which are related to coarse particles. Bulk collection methods at Montseny were considered representative of total atmospheric deposition, since bulk deposition plus DAR accounted for 97% of total deposition measured with wet and dry-only collection devices. Thus, bulk deposition collectors can be recommended for deposition networks at remote sites (lacking electricity connection) in environments, where coarse particles are a predominant fraction of the aerosol mass.

Key words: atmospheric input, bulk deposition, wet deposition, dry deposition, precipitation chemistry, Mediterranean region

1. Introduction

Atmospheric deposition contributes to the chemistry of plants, soils and surface water, and to the cycling of nutrient in ecosystems (Richter and Lindberg, 1988). Wet and dry deposition are efficient pathways for removing soluble gases and particles from the atmosphere. Wet deposition is defined as the process by which gases and aerosols are incorporated into cloud droplets, either as forming cloud condensation nuclei, or being incorporated in cloud droplets or scavenged as the droplets fall to the ground (Seinfeld and Pandis 1998). Wet deposition is delivered to the earth's surface in the form of rain, snow and mist (Chantara and Chunsuk 2008). Dry deposition of gases and particles occurs by turbulent transfer and by gravitational settling on land and over water surfaces (Lovett 1994). Several studies consider wet precipitation as the most effective scavenging factor for removing particulate and organic and inorganic gaseous pollutants from the atmosphere (Al-Khashman 2009; Arsene et al. 2007; Prathibha et al. 2010), but dry deposition may have a higher contribution in arid environments as precipitation becomes scarce (Dolske and Gatz 1985; Guerzoni et al. 1999; Aas et al. 2009).

The concentrations of chemical species in precipitation vary widely in depending on different factors: type and distribution of aerosol sources, transport, chemical species and scavenging processes (Celle-Jeanton et al. 2009). Moreover, it has long been recognized that the method used for the collection of precipitation samples for chemical analysis can have a significant effect on the results (Galloway an Likens 1978; Sisterson et al. 1985; Dämmgen et al. 2005; Cape et al. 2009; Kelly et al. 2012). Wet deposition is sampled by using a collector which has a removable lid that covers a collecting bucket or funnel to exclude dry deposition during the dry periods and opens whenever precipitation is detected by means of a precipitation sensor (Plaisance et al. 1998; Dämmgen et al. 2005; Staelens et al. 2005). However, in many ecological studies precipitation often is collected by a bulk collector which consists of an open funnel (glass or plastic) connected to a sampling bottle (Erisman et al. 2003). This sampling method does not require power supply and it allows for an efficient operation in remote sites lacking electricity connection (Cape et al. 2009). It is also highly cost-effective for implementation in large networks.

Chemical differences have been reported between sampling methods: in most cases, deposition to the bulk collectors is significantly greater than to wet-only collectors with exception of free acidity (H^+) and ammonium (NH_4^+) (Staelens et al. 2005; Cape et al. 2009). On the one hand, the physical properties of the samplers, such as differences in flow distortion or a high evaporation rate from the sampling funnel are likely to play an important role (Dämmgen et al. 2005). However, differences between bulk and wet-only deposition are mainly attributed to the contribution of the dry deposition flux (Galloway and Likens 1976; Fowler and Cape 1984; Draaijers et al. 1998; Akkoyunlu and Tayanc 2003; Anatolaki and Tsitouridou 2007). Because bulk collectors are permanently open to the atmosphere, there is a dryfall flux previous to the rain that is incorporated into the rainwater as rain washes the funnel walls.

Dry deposition is governed by several processes such as the element concentration in air, turbulent transport processes in the atmospheric boundary layer, gravitational settling (for sufficiently large particles), molecular diffusion or other transport processes near the surface, the chemical and physical nature of the depositing species, and the capability of the surface to capture and absorb gases and particles (Erisman et al. 1994). Therefore, the accurate estimation of dry deposition involves an understanding of several influential variables including the atmospheric characteristics, the nature of the surface and the properties of the depositing species itself (Davidson and Wu 1990). In fact, there is not a standard method for the measurements of dry deposition. Dry deposition has been often inferred from the product of the measured species in ambient concentrations and its dry deposition velocity (Duce et al. 1991; Erisman et al. 1998; Guerzoni et al. 1999; Migon et al. 2001; Anatolaki and Tsitouridou 2007), by means of statistical models (Dulac et al. 1989; Erisman et al. 1994; Brook et al. 1997; Yi et al. 1997; Staelens et al. 2008) or through micrometeorological approaches (Erisman and Draaijers 1995; Wesely and Hicks 2000). Still, a routine direct measurement technique is required for validating these estimates (Sakata et al. 2008).

Direct measurements have included: 1) collection on dry-only collectors (Rao et al. 1992; Morales-Baquero et al. 2006; Pulido-Villena et al. 2008; Al-Momani et al. 2008), 2) collection on surrogate plant surfaces (Ferm and Hultberg 1999; Sanz et al. 2002; Moumen et al. 2004; Inomata et al. 2009) and 3) throughfall (Parker 1983; Lovett 1994). To better mimic the transport to water bodies and moist landscapes, in some studies the surface of sampler is wetted (Shahin et al 1999; Azimi et al. 2003; Anderson and Downing 2006). Also, measurements by electron microscope counting, wind-tunnel studies and chamber studies have been used to estimate dry deposition (Erisman et al. 1994). Since some chemical elements characteristically can occur in the atmosphere as large particles, small particles, gases or a combination of these, different methods are needed for different elements (Lovett, 1994). Despite the difficulties associated with the dry deposition measurement, the methods here described have been widely used for the quantification of deposition of the coarse aerosol fraction (Guerzoni et al. 1999; Morales-Baquero et al. 2006; Pulido-Villena et al. 2006).

In the western Mediterranean basin the contribution of dry deposition to the total deposition flux has received little attention, despite the frequent impact of African dust outbreaks contributing to the build up of particles and pollutants in the atmosphere (Querol et al. 1998; Rodríguez et al. 2001; Escudero et al. 2005), stagnant summer air producing an accumulation of pollutants (Millán et al. 1997; Rodríguez et al. 2002) and long spells of dry weather in summer (and sometimes also in winter), all suggesting that dry deposition may have an important role in this region. The aerosol composition in NE Spain is dominated by the crustal component composed of coarse sized particles (Pérez et al. 2008; Pey et al. 2009, Querol et al. 2009) which are predominantly deposited by gravitational sedimentation, thus they can be correctly captured by open collectors (Lindberg et al. 1986).

In this study we determined the chemical signature of wet-only, dry-only and bulk deposition and quantified their fluxes at a rural site in the Montseny mountains (NE Spain). Total deposition was assessed as the sum of wet-only plus dry-only deposition or by the sum of bulk plus any dryfall occurred after the rain (named DAR). The DAR specific analysis was devised because of the need to evaluate the magnitude of this flux. Since DAR mostly collects coarse particles that fall by gravitation, one can suspect that it will be more important in dry climates. Here, we make a contribution to the literature by measuring the DAR contribution in a forested rural area in a sub-humid meso-Mediterranean climate (Rodà et al 1999).

Two procedures for total (mostly gravitatory) deposition were compared: dry only+wet only and bulk+DAR collectors. The chemical signatures of water collected from them were studied and the deposition fluxes were evaluated to characterize their magnitude and evaluate their relative contribution to total deposition. This has a practical outcome since, if a good equivalence were obtained, the bulk deposition method would provide the advantage of being a very cost-effective procedure that can be deployed in remote environments independent of electric supply.

The methodology employed here is useful to evaluate dry and wet fluxes on bucket or funnel-type collectors usually in use in atmospheric deposition monitoring programs, but for an assessment of nutrient inputs to ecosystems and to the landscape, this methodology does not properly take into account the flux deposition of gases and fine aerosols. For a total quantification of nutrient deposition to ecosystems, other methodologies addressing gas and fine aerosol deposition must be included, such as throughfall sampling or gas and fine particle deposition modelling.

2. Material and methods

2.1. Study site

Deposition was weekly sampled at La Castanya (LC, 41º46'N, 2º21'E, 700 m above sea level (m.a.s.l.), located in the Montseny mountains of the Pre-litoral Catalan Range (Fig.1). Since 2002 the station has been instrumented as a background regional air quality site (Pérez et al. 2008, Pey et al. 2009). The site is amidst extensive holm oak (*Quercus ilex* L.) forests in the Montseny Natural Park, 40 km to the N-NE from Barcelona and 25 km from the Mediterranean coast (Fig. 1). Since the late 70s it provides deposition data for long-term biogeochemical studies that have been undertaken in a close holm-oak forest plot (Rodà et al. 1999).

Agricultural and sylvo-pastoral activities extend into the surroundings. The lithology of Montseny is mainly composed of schists and granodiorites.

The climate in Montseny is meso-Mediterranean sub-humid, with high interannual variability in precipitation, ranging from 503 to 1638 mm y^{-1} (period 1983-2009; mean: 840 mm y^{-1} at LC). Summer droughts are common, though often attenuated by frequent orographic storms. Mean air temperature at LC was 9ºC during the period 1983-2000. During the coldest season, the LC station is usually outside the mixing layer and is therefore less affected by regional anthropogenic pollution, however, during specific anticyclonic conditions which are common in summer and winter, highly polluted air masses from the coast and valleys are transported towards LC by mountain/sea breezes (Pérez et al. 2008).

2.2. Sampling and chemical analysis

From February 2009 to July 2010 two different collector systems typically used in monitoring programs and ecological studies (bulk and dry/wet collectors) were weekly sampled in parallel. A standard rain gauge (Hellman) was used to measure weekly precipitation. Bulk deposition was collected in 2 open collectors (Fig. 2a) placed at 1.5m above the ground. The collectors were designed as in Likens et al. (1977), and consisted of a polyethylene funnel of 19cm diameter connected by a tygon looping tube to a 10-L polyethylene bottle, with a nylon sieve stopper in the neck of the funnel to prevent contamination from insects and plant debris. In addition, dryfall after the last rain (hereafter, DAR) was collected by rinsing the funnel walls with 250ml of deionized distilled water during each weekly visit. Afterwards, bulk deposition collectors were retrieved and replaced by a clean sampling kit. Cleaning procedures for funnels, tubes and buckets included repeated washes in the laboratory of all the material with deionized distilled water until electrical conductivity of the rinse was ~ 1 μS cm^{-1}.

Wet-only and dry-only was sampled with an Andersen device (ESM Andersen instruments, G78-1001; Fig. 2b). The collector was equipped with two polyethylene buckets (29cm inner diameter) and a shutting lid which covered the wet bucket but was moved to cover the dry one at the beginning of each rain event; after the end of the rain (20min) it returned to the previous position. Weekly wet samples were transferred into clean 250ml polyethylene bottle. Weekly dry deposition was recovered by rinsing the collection bucket with 250ml deionized water and transferred to a clean 250ml polyethylene bottle. Wet and dry buckets were cleaned in the field with repeated washes with deionized water and blanks were taken on a regular basis. If any contamination (e.g. bird droppings, plant debris) was detected, samples were rejected. Samples were taken to the laboratory and processed according to previously described protocols (Àvila 1996; Àvila and Rodà 2002). pH, alkalinity, and the concentrations of Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+, Cl^-, NO_3^- and SO_4^{2-} were measured. Within 48h of sampling, alkalinity and pH were measured in unfiltered samples and 60ml aliquots were filtered through 0.45μm size pore membrane filter and frozen (-20ºC) before analysis. Ion chromatography was used for Na^+, K^+, Mg^{2+}, Ca^{2+}, NH_4^+ Cl^-, NO_3^- and SO_4^{2-} (Dionex, Sunnyvale, USA). Data quality was evaluated by (1) the use of control solutions (synthetic solutions prepared in the laboratory with known ionic concentrations) during all analytical runs, and (2) an ionic ratio (cation sum/anion sum) accepting a 20% variation about the central value (= 1.00). For DAR and dry-only samples a 30% allowance was accepted because of the very low concentrations in these solutions. Results of the quality indexes are shown in Table 1.

Volume weighted mean (VWM) concentrations were calculated with the Hellman rain gauge precipitation measures. Deposition fluxes were obtained as the product of VWM concentrations by precipitation volume (Hellman) in the study period. For dry and DAR, deposition was calculated as the product of arithmetic mean concentrations by the volume of washing solution (250ml). Wet-only, dry-only, bulk and DAR deposition fluxes are expressed as annual deposition values.

Total deposition is defined as the sum of wet-only and dry-only deposition recorded in the samplers. Here, the total deposition was estimated using measures from two different sampling methods: 1) the sum of separate dry-only and wet-only measures, and 2) the sum of bulk deposition plus DAR and both methods were compared.

We have to acknowledge that “dry fall” collectors, such as dose used here, are not well suited for components with an important gaseous phase or for fine particles such as sulphate aerosols (Dasch 1985; Davison and Wu, 1990; Zobrist et al. 1993); thus for a regional assessment of nutrient inputs to ecosystems at the landscape scale, supplementary methods for gaseous and fine particle deposition should be considered.

2.3. Statistical analyses

Wilcoxon tests, linear regressions and Spearman correlations (the appropriate statistic for non-normal distributions) were computed with Statistica™. The coefficient of determination (r^2) has been used to compare the different sampling methods. Spearman correlation (ρ) has been used to describe the relationships between ions within each type of sampling method. Arithmetic means are accompanied with standard deviation (SD). Only 2% of bulk and wet deposition samples and 14% of dry deposition samples were excluded from the data base because of observed funnel or bucket contamination (e.g. bird droppings or plant debris).

3. Results

3.1. Amount of precipitation

In the study period (February 2009-July 2010), 98% of the samples corresponded to rain, the rest corresponding to mixed rain and snow. Weekly precipitation volume collected with the Hellmann rain gauge ranged from 2.4 to 149 mm, with a mean (±SD) of 29.4±28.6 mm. Hellmann weekly amounts were 6% and 9% higher than bulk and wet-only collectors respectively (p<0.01). A good correlation was observed between the Hellmann rain gauge and the other sampling devices (r^2=0.99).

Precipitation amount collected in bulk and wet-only collectors also showed significant differences in the Wilcoxon test (p<0.01, Table 2). Bulk collection efficiency was 3.2% higher than wet-only. Also, a high correlation (r^2=0.99; Table 2) between the both collector types was found.

3.2. Wet-only and bulk deposition chemical signature

The chemical composition of 47 wet-only and bulk precipitation samples obtained from February 2009 to July 2010 was used in this comparison (Table 2).

The Wilcoxon signed-rank test showed weekly bulk concentrations to be significantly (p<0.05) higher than wet-only concentrations for Na^+, Ca^{2+}, Mg^{2+}, Cl^- ,NO_3^- and SO_4^{2-}, while the reverse was true for NH_4^+ (Table 2). No significant differences were found for alkalinity and H^+ concentrations.

Regression analysis for the chemical constituents in bulk *vs.* wet-only samples indicated high coefficients of determination (r^2 >0.75) ordered by this rank: $Ca^{2+} > Na^+ > Cl^- > SO_4^{2-} > Mg^{2+} >$ alkalinity > NO_3^-. Ammonium showed moderate coefficients of determination (r^2 =0.64), and K^+ and H^+ concentrations, low (r^2~0.4) but still significant (p<0.001; Table 2).

It should be noticed that VWM concentrations (Table 3) were lower than the arithmetic mean concentrations (Table 2) indicating that higher concentrations are associated with lower rainfalls. This is due to the scavenging of the below-cloud atmosphere by the first drops of rainfall that present the highest concentrations with low precipitation amount and the exhaustion of pollutants as precipitation proceeds (Colin et al. 1989; Beverland et al. 1998; Prado-Fiedler, 1990; Kelly et al. 2012).

The pH of wet-only and bulk precipitation ranged between 4.7 and 7.4 (the maximum range was for wet-only deposition). Such co-occurrence of acidic and alkaline rains within the averaging period precludes the use of the conventional method of computing VWM precipitation pH from VWM H^+, because H^+ is not conservative (Escarré et al. 1999). Instead alkalinity is the conservative property to average: assuming that bicarbonate accounts for most of the alkalinity and using the constants of the carbonate-bicarbonate equilibrium, the average pH can be calculated (Liljestrand 1985; Young et al. 1988). Because of similar alkalinities in bulk and wet only deposition (Table 3) the resultant VWM pH was 6.4 for both sample types.

Based on the VWM, the predominant anions were NO_3^- and SO_4^{2-} with mean concentrations of 20-23 μeq L^{-1} and 18-20 μeq L^{-1} in wet and bulk deposition, respectively (Table 3). The predominant cations were Ca^{2+} and NH_4^+ which constituted about 73-80% of the sum of cations in wet-only and bulk samples (VWM concentrations 27-38 μeq L^{-1} and 22-30 μeq L^{-1}, respectively; Table 3).

Spearman rank correlations between the measured ions in bulk (Fig. 3a) and wet-only (Fig. 3b) deposition were calculated to understand the different processes affecting them. Both sample types showed similar patterns characterized by: (1) significant high correlations ($\rho \geq 0.80$; $p<0.05$) between compounds from the same origin, marine (Na^+ and Cl^-) and crustal compounds (Mg^{2+}, Ca^{2+}, and partially SO_4^{2-}), and between NO_3^- and crustal compounds, except for the wet-only NO_3^--Mg^{2+} correlation which, nonetheless, was close ($\rho=0.78$); (2) close correlations ($0.80>\rho \geq 0.60$; $p<0.05$) between components which usually constitute fine particles (NO_3^-, NH_4^+ and partially SO_4^{2-}), and between Mg^{2+} *versus* marine compounds in both sample types, *versus* K^+ in bulk samples and *versus* NO_3^-- in wet-only samples. In wet-only samples the correlation between NO_3^- and NH_4^+ ($\rho=0.77$) was higher than in bulk samples ($\rho=0.47$), conversely, the correlation between Na^+ and Ca^{2+} was lower ($\rho=0.54$ *vs*. 0.66). The rest of correlations showed coefficients lower than 0.6 (Fig. 3).

3.3. Dry-only deposition chemical signature

The arithmetic means for alkalinity and ion concentrations in dry deposition are shown in Table 4. The highest mean ion concentration was for Ca^{2+} with 126 ± 70.8 μeq L^{-1} and the rest of them were ordered (descending order): alkalinity > NO_3^- > SO_4^{2-} > Na^+ > Cl^- > Mg^{2+} > K^+ > NH_4^+.

Spearman rank correlations in dry-only deposition samples (Fig. 3c) were different from those observed in wet-only deposition samples (Fig. 3b). The relationship between crustal compounds (Mg^{2+}, Ca^{2+} and partially SO_4^{2-}) and between those and NO_3^- decreased in dry-only samples, conversely it increased for SO_4^{2-} *versus* sea-salt ions and K^+ *versus* Mg^{2+} and SO_4^{2-}. Non significant correlations were observed for NH_4^+.

3.4. Total deposition fluxes

Co-located bulk and wet/dry samplers allowed the calculation of deposition fluxes in both collector types and to compare their collection efficiency. For bulk deposition fluxes, DAR was also collected and added. We considered that wet+dry should be equivalent to bulk+DAR fluxes and these corresponded to total deposition (Fig. 4 and Table 5). The sum fluxes of measured ions for the bulk+DAR was similar to that of wet+dry (27.0 *vs.* 27.8 kg ha^{-1} yr^{-1}). For individual ions, differences between the sampling methods (referred to wet+dry deposition) were <7% for Ca^{2+}, Mg^{2+}, NO_3^--N, SO_4^{2-}-S and Na^+, while for NH_4^+-N, K^+ and Cl^- they were >15% (Fig. 4). The NH_4^+-N wet+dry deposition flux was higher (3.90 kg ha^{-1} yr^{-1}) than bulk+DAR (2.71 kg ha^{-1} yr^{-1}). For K^+, the wet+dry flux was 18% higher than the bulk+DAR flux (1.63 and 1.33 kg ha^{-1} yr^{-1} respectively). Conversely, for marine ions the wet+dry flux was lower than the bulk+DAR: 15% for Cl^- (4.57 *vs.* 5.26 kg ha^{-1} yr^{-1}) and 7% for Na (2.71 *vs.* 2.90 kg ha^{-1} yr^{-1}). Linear regressions between both total deposition estimates showed significant correlations ($r^2 \geq 0.65$, p<0.001) for all ions, except for K^+ (r^2=0.42, p=0.003).

The sum fluxes of the measured ions for the bulk annual deposition accounted for 89% (24.8 kg ha^{-1} yr^{-1}) of the wet+dry flux. For individual chemical species, except for K^+ and NH_4^+-N which represented ~70% (Table 5), it accounted >80% of the sum wet+dry flux. The fraction of deposition which is recovered in bulk collectors after the last rain (DAR) is only 8% (2.21 kg ha^{-1} yr^{-1}) of the wet+dry flux. For individual ions, it accounts 6-13% for ions associated with coarse particles (Na^+, Cl^-, Ca^{2+}, Mg^{2+}, K^+) and 2-5% for fine particles (NH_4^+-N, NO_3^--N, SO_4^{2-}-S, Table 5).

Wet annual deposition contributed to 74% of total (wet+dry) deposition in the study (Table 5). Even if dry deposition only accounted for 26% of wet+dry deposition, it was relatively more important for K^+, Ca^{2+} and Mg^{2+} with ~45% (0.76 kg ha^{-1} yr^{-1}), ~40% (3.26 kg ha^{-1} yr^{-1}) and ~35% (0.27 kg ha^{-1} yr^{-1}) respectively of the wet+dry flux. Conversely, NH_4^+-N dry deposition only represented 5% (0.18 kg ha^{-1} yr^{-1}) of total NH_4^+-N deposition (Table 5).

The contributions of wet and dry to wet+dry deposition for two different sampling periods at LC are shown in Table 6. The wet+dry annual deposition in 2002-2003 was almost twice that of 2009-2010 (49.5 and 27.8 kg ha^{-1} yr^{-1} respectively). Despite this big difference, which is attributed to a higher contribution of African air masses in 2003 (19% vs. 6% in 2009-2010), the percentages of wet deposition for each chemical species to the sum wet+dry deposition were similar for both periods (Table 6).

4. Discussion

4.1. Amount of precipitation

Bulk and wet deposition are calculated as the product of representative concentrations (usually VW means) and the amount of precipitation. Precipitation amount should be measured with standard rain gauges because the collection efficiency of precipitation samplers is influenced by disturbance of the airflow over and around a collector, height above the ground, evaporation of collected rainwater and, in the case of wet-only collectors, the efficiency of rain sensors (Stedman et al. 1990). The Hellman sampler is considered as a standard rain gauge for the measurement of precipitation (Sevruk and Klemm 1989) with an error of 7% (German standard DIN 58666, 1966). Regression analysis of precipitation amount indicates that bulk and wet-only deposition samplers showed good agreement with the Hellmann rain gauge in this study. However, the Hellman gauge collected higher amounts than bulk and wet-only collectors (6% and 9% respectively). A similar pattern was observed in Thailand, where bulk and wet-only deposition collectors collected 2.0% and 0.3% less than the standard rain gauge, respectively (Chantara and Chunsuk 2008). For 20 countries participating in a European study, significant differences were reported between the rain gauge value and the best estimate of bulk deposition and wet-only deposition (Erisman et al. 2003). Unlike our results, the precipitation volumes collected in their study were systematically higher in bulk and wet-only samplers compared to the Hellmann rain gauge (15 and 5% respectively, Erisman et al. 2003).

The precipitation volume collected in bulk deposition samplers was significantly higher than in the wet-only bucket (Table 2), similarly as reported by other authors (Stedman et al. 1990; Thimonier 1998; Balestrini et al. 2000; Erisman et al. 2003; Cape et al. 2009). This difference is attributed to differences in device structure (Draaijers et al. 1998) and to the delayed opening of the lid at the onset precipitation (Stedman et al. 1990; Erisman et al. 2003; Kelly et al. 2012)

4.2. Wet-only and bulk deposition chemical signature

Bulk precipitation chemistry at Montseny was characterized by a positive alkalinity with most of the potential acidity of strong acids being neutralized by calcium bicarbonate and NH_3 (Table 3). Since bulk deposition includes both wet and some dry deposition, the concentration of chemical components in bulk deposition was higher than in wet-only samplers, as also found in other studies (Akkoyunlu and Tayanc 2003). Wilcoxon signed-rank tests indicated that all ion concentrations (except NH_4^+) were significantly higher in bulk than wet-only precipitation; for alkalinity and H+, differences were non-significant (Table 2). A greater enhancement in bulk deposition of soil-derived ions from large wind-blown particles such as Ca^{2+}, Mg^{2+}, K^+, sometimes SO_4^{2-} and sea-salt ions (Na^+, Mg^{2+}, Cl^-) is observed, which is akin to results of other studies (Thimonier 1998; Erisman et al. 2003; Akkoyunlu and Tayanc 2003; Staelens et al. 2005; Pelicho et al. 2006; Cape et al. 2009). The concentrations of NH_4^+ in the wet-only samples were noticeably higher than in the bulk samples (ratio bulk/wet-only = 0.74, Table 3). Reasons for higher NH_4^+ concentrations in wet-only samples are not well determined for the time being. Other authors sampling wet and bulk deposition had found a similar result which has been attributed to: 1) N-species, being in general unstable, decomposing under high temperatures while sitting in the field before collection; because of collector design, higher temperatures could affect bulk collectors (Anatolaki and Tsitouridou 2007; 2) higher biological degradation in a continuously-open sampler (Cape et al. 2009). We propose another mechanism to explain this difference: a loss of NH_4^+ by evaporation/re-emission of NH_3 from the bulk collector, especially as pH may increase on storage by carbonate dissolution, thereby pushing the equilibrium towards higher pH.

Ions associated with coarse particles (soil-derived -Ca^{+2}, Mg^{+2}, partially SO_4^{-2}- and sea salt ions -Cl^-, Na^+ and partially Mg^{+2}) showed the highest correlations between bulk and wet-only samples (Table 2), suggesting that bulk and wet-only samples collected ions from the same source and chemical form. The different behaviour of K^+ could be attributed to particulates of biological origin, such as pollen, small vegetation fragments or ash from biomass burning, deposited on the bulk surface at certain times of year but not reaching the lidded wet collector (Likens et al. 1994; Balestrini et al. 2007; Praveen et al. 2007).

Spearman correlations between ion concentrations (Fig. 3a,b) provided some information on the sources of ions collected in bulk and wet-only samples separately. Both sample types showed high correlations between coarse particles: the Na^+ and Cl^- correlation indicated the marine influence received at LC which is located at 25 Km from the Mediterranean coast; Ca^{2+}, Mg^{2+} and SO_4^{2-} correlations can be in part attributed to the dissolution of African mineral dust due to the usual occurrence of mineral dust plumes from Africa over the Iberian Peninsula (Rodríguez et al. 2001; Escudero et al. 2005; Moreno et al. 2005). Correlations between marine and crustal compounds may indicate the incorporation of marine aerosols into clouds as the air mass trajectory crosses over the Mediterranean from North Africa to NE Spain. Accordingly, previous studies at Montseny have found very high concentrations of marine and crustal components in African rains compared to rains of other provenances (Àvila et al. 1997). Correlations between NH_4^+, NO_3^- and SO_4^{2-} are usually related with anthropogenic emissions and high pollution levels (Saxena et al. 1997; Tanner 1999; Praveen et al. 2007). Additionally, the good correlation observed among NO_3^- and Na^+ and Ca^{+2} can be associated with the formation of secondary coarse $NaNO_3$ and $Ca(NO_3)_2$ aerosols originating from the interaction of HNO_3 and sea salts and calcite ($CaCO_3$) during warm periods when NH_4NO_3 is thermically unstable (Harrison and Pio 1983; Pakkanen 1996; Querol et al. 1998).

4.3. Dry-only deposition chemical signature

The chemistry of dry deposition samples at La Castanya (Table 4) was dominated by Ca^{2+} concentrations. This, together with relatively high concentrations of the other base cations (K^+, Na^+, Mg^{2+}) provided the observed high alkalinity (74.0 ± 45.9 μeq L^{-1}) and pH (6.50 ± 0.72) of these samples. In dry deposition, NO_3^- (34.6μeq L^{-1}) predominated over NH_4^+ (10.2μeq L^{-1}) which can result from NH_4^+ volatilization, biological NH_4^+ consuming process as mentioned for the bulk samples, or to fine NH_4^+ containing aerosols and NH_3 gases not being dry deposited by sedimentation. These results are within the range of ion concentrations in dry deposition observed in Italy (Balestrini et al. 2000) though in this study NH_4^+ concentrations (6-76μeq L^{-1}) were higher than NO_3^- (9-46 μeq L^{-1}).

A close correlation was observed between marine components (Na-Cl r=0.91; p>0.05; Mg^{2+}-Na^+ and Cl^-, 0.80 <ρ> 0.60) for all deposition types, confirming the sea salt influence in wet and dry deposition (Fig 3). However, for other components, correlations differed between deposition types: e.g. Ca^{2+} and NO_3^- showed high correlations only in dry deposition. Taking into account that dry deposition is size dependent (Koçak et al. 2010) this suggests dry deposition of coarse $Ca(NO_3)_2$ onto dry collectors. Sulphate showed stronger correlations with Ca^{+2} and Mg^{2+} in wet than in dry, suggesting that other sources of Ca^{+2} and Mg^{2+} (Ca and Mg carbonates) have a higher contribution to dry than to wet deposition.

4.4. Total deposition fluxes

This study demonstrated that sum flux of all measured ions in the bulk+DAR flux accounted for 97% of the wet+dry flux (Table 5). Differences between both methodologies for Ca^{2+}, Mg^{2+}, NO_3^--N, SO_4^{2-}-S and Na^+ were <7% (Fig. 4; Table 5). A good correlation between bulk and wet collecting methods was found for all chemical species, except for K^+ (Table 2). Small differences can be attributed to the uncertainty associated to collection catch; however, the lower NH_4^+ and K^+ values in bulk deposition (30% and 18%, respectively) probably result from biological interactions such as NH_4^+ consumption from microorganisms in bulk samplers, and contamination with biological particles in dry deposition samplers.

Bulk deposition (sum of all measured ions) accounted ~ 90% of the wet+dry flux and more than 80% of individual chemical species, except for K^+ and NH_4^+-N (Table 5). For K^+ and NH_4^+ our results concur with many other studies to indicate that deposition estimates for these ions should be interpreted with caution since biological interactions may occur (Draaijers et al. 1998; Balestrini et al. 2002; Cape et al. 2009). DAR was higher for coarse particle-derived elements (6-13%) than for fine particle-derived (2-5%; Table 5). The bulk+DAR flux at Montseny accounted 97% of wet+dry deposition. Given the advantages for bulk sampling in remote sites, the sum of bulk plus DAR can be recommended for extensive low cost sampling in comparable environments in the Mediterranean with the provision that K^+ and NH_4^+ have higher uncertainty.

Dry deposition was dominated by Ca^{+2}, Mg^{+2} and K^+ which accounted for 40, 35 and 45% of the total deposition. These values were close to percentages observed in other locations of the Mediterranean such as northern Italy (Balestrini et al. 2000; 41-60, 35-64 and 57-67%, respectively) or southern France (Celle-Jeanton et al. 2009; 36, 24 and 46% respectively), but lower than in Sierra Nevada (South Spain) where Ca^{+2} dry deposition was 64% of total deposition (Pulido-Villena et al. 2006). The higher influence of Saharan dust inputs and the lower rainfall amount in southern Spain may explain higher Ca^{2+} dry deposition in Sierra Nevada.

Dry deposition for SO_4^{2-}-S (~17% of ionic sum), NO_3^--N (~20%) and NH_4^+-N (5-18%) was in accordance with percentages reported in Italy and France with similar sampling methodologies (14-50% for SO_4^{2-}-S; 15-31% for NO_3^--N; 1-37% NH_4^+-N; Possanzini et al. 1988; Balestrini et al. 2000, 2002; Celle-Jeanton et al. 2009). In dryer climates such as Greece and the Eastern Mediterranean, dry deposition was the main source of NO_3^--N (75-90%; Anatolaki and Tsitouridou 2007; Al-Momani et al. 2008; Koçaç et al. 2010) and SO_4^{2-}-S (55-63%; Anatolaki and Tsitouridou 2007; Al-Momani et al. 2008).

5. Conclusions

At Montseny (NE Spain) total deposition estimated by wet+dry and bulk+DAR showed differences <15%, except for K^+ and NH_4^+. Results for ammonium highlight the difficulties of studying biologically labile species. For K^+, deposition of biological components such as pollen, ash and small plant debris is suggested.

The removal of atmospheric compounds occurred mainly by wet deposition, which contributed 74% of total wet+dry deposition in this semi-humid Mediterranean climate. Dry deposition was characterized by the predominance of crustal ions such as Ca^{2+} and Mg^{2+} or crustal-biological such as K^+. Although dryfall after the last rain (DAR) only contributed 8% of the sum of all ions in wet+dry deposition, this was an important measurement to include, since bulk deposition plus DAR accounted for 97% of wet+dry deposition Thus, in Mediterranean rural environments, when field conditions do not favour the deployment of wet and dry-only devices, bulk plus DAR measurements can be implemented to represent total fallout deposition.

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Table 1. Data quality: Results of reference sample replication and average of the quality control index (cation sum/anion sum) calculated for type of measurement. DAR= rinse of the bulk collector walls after the last precipitation.

	n	Reference solution (μeq/L)	Analysed value Mean ± s.e (μeq/L)
Na^+	9	50	55.3 ± 1.36
K^+	9	10	11.0 ± 0.34
Ca^{2+}	9	100	107 ± 2.47
Mg^{2+}	4	32	33.8 ± 1.57
Mg^{2+}	5	25	25.8 ± 1.27
NH_4^+	4	40	43.2 ± 2.39
NH_4^+	5	50	52.5 ± 4.43
NO_3^-	15	18	18.4 ± 0.48
SO_4^{2-}	15	40	40.3 ± 0.68
Cl^-	15	20	21.1 ± 0.52
Index Σcations/Σanions	**n**	**Theoretical value**	**Mean ± Standard Error**
Bulk	47	1,00	1.10 ± 0.02
Wet-only	47	1,00	1.15 ± 0.01
Dry-only	40	1,00	1.10 ± 0.02
DAR	43	1,00	1.14 ± 0.03

Table 2. Descriptors (range, arithmetic mean and standard deviation) of the chemical composition of bulk and wet-only samples at La Castanya (Montseny) for the period February 2009-July 2010. Significance level of the differences according to the Wilcoxon signed-rank test and R^2 for linear regressions between bulk and wet measurements are also given.

			Bulk				Wet-only				Wilcoxon test	Linear regressions
		n	Min.	Max.	A.mean	S.D	Min.	Max.	A.mean	S.D	*p*-value	r^2
Rain	(mm)	41	2.24	154	27.6	28.0	1.89	151	26.8	27.6	<0.01	0.99^{***}
Alkalinity	(μeq L^{-1})	47	-8.33	237	32.4	42.0	-20.6	559	35.3	83.7	0.36	0.77^{***}
H^+	(μeq L^{-1})	47	0,07	8,91	1,98	2,18	0,04	20,9	2,43	3,66	0.76	0.43^{***}
Na^+	(μeq L^{-1})	47	2.99	89.4	14.7	15.2	1.80	78.7	11.0	12.5	<0.01	0.91^{***}
K^+	(μeq L^{-1})	47	0.66	17.7	4.14	3.29	0.50	14.6	3.27	2.83	<0.05	0.39^{***}
Ca^{2+}	(μeq L^{-1})	47	5.39	609	71.7	97.3	5.05	723	56.6	111	<0.01	0.93^{***}
Mg^{2+}	(μeq L^{-1})	47	0.84	61.3	10.1	10.7	0.93	63.0	7.22	9.34	<0.01	0.82^{***}
NH_4^+	(μeq L^{-1})	47	1.62	129	27.8	26.7	3.44	126	40.2	27.5	<0.01	0.64^{***}
NO_3^-	(μeq L^{-1})	47	5.29	167	35.5	31.0	3.49	161	33.5	30.7	<0.05	0.76^{***}
SO_4^{2-}	(μeq L^{-1})	47	6.10	138	27.7	21.3	4.40	151	26.1	23.4	<0.05	0.86^{***}
Cl^-	(μeq L^{-1})	47	3.64	103	16.3	17.5	2.20	78.2	10.8	12.8	<0.01	0.91^{***}

$^{***}p<0.001$

Table 3. Volume-weighted mean (VWM) concentrations for the analysed chemical species (units in μeq L^{-1}) and ratio of the VWM bulk and wet concentrations at La Castanya (Montseny) for the period April 2009-July 2010.

	Bulk	Wet-only	Ratio (bulk/wet-only)
Alkalinity	17.7	17.1	1.03
pH	6.45	6.43	1.00
Na^+	13.1	9.89	1.33
K^+	3.27	2.38	1.37
Ca^{2+}	38.2	27.2	1.41
Mg^{2+}	6.36	4.69	1.36
NH_4^+	22.3	30.2	0.74
NO_3^-	22.7	20.3	1.11
SO_4^{2-}	19.8	18.0	1.10
Cl^-	15.6	10.8	1.44

Table 4. Descriptors (range, arithmetic mean and standard deviation) of the chemical composition of dry-only samples at La Castanya (Montseny) for the period April 2009-July 2010. Concentrations in μeq L^{-1}.

		Dry-only				
		n	Min.	Max.	A.mean	S.D
Alkalinity	(μeq L^{-1})	43	12.9	172	74.0	45.9
H^+	(μeq L^{-1})	43	0.005	3.98	0.74	0.85
Na^+	(μeq L^{-1})	43	2.77	134	21.7	26.1
K^+	(μeq L^{-1})	43	1.50	56.2	15.0	15.5
Ca^{2+}	(μeq L^{-1})	43	29.3	325	126	70.8
Mg^{2+}	(μeq L^{-1})	43	4.93	44.7	17.0	9.87
NH_4^+	(μeq L^{-1})	43	0.70	89.7	10.2	17.1
NO_3^-	(μeq L^{-1})	43	0.71	106.8	34.6	25.8
SO_4^{2-}	(μeq L^{-1})	43	6.07	99.0	26.4	19.0
Cl^-	(μeq L^{-1})	43	3.27	142.2	22.9	28.3

Table 5. Annual deposition (in kg ha^{-1} yr^{-1}) for the different considered fluxes from April 2009 to July 2010. Percentages relative to total (wet+dry) are also indicated.

Annual deposition	Bulk	DAR	Bulk+DAR	Wet-only	Dry-only	Wet+dry
Na^+	2.73 (101%)	0.16 (6%)	2.90 (107%)	2.07 (76%)	0.64 (24%)	2.71
K^+	1.13 (69%)	0.20 (12%)	1.33 (82%)	0.87 (54%)	0.76 (46%)	1.63
Ca^{2+}	7.06 (86%)	1.10 (13%)	8.16 (100%)	4.92 (60%)	3.26 (40%)	8.18
Mg^{2+}	0.70 (92%)	0.09 (11%)	0.78 (104%)	0.49 (65%)	0.27 (35%)	0.76
NH_4^+-N	2.64 (68%)	0.08 (2%)	2.71 (70%)	3.71 (95%)	0.18 (5%)	3.90
NO_3^- -N	2.78 (91%)	0.14 (4%)	2.92 (96%)	2.42 (79%)	0.62 (21%)	3.04
SO_4^{2-} -S	2.82 (93%)	0.16 (5%)	2.98 (98%)	2.48 (82%)	0.55 (18%)	3.03
Cl^-	4.98 (109%)	0.28 (6%)	5.26 (114%)	3.52 (77%)	1.05 (23%)	4.57
Ion sum	24.83 (89%)	2.21 (8%)	27.04 (97%)	20.48 (74%)	7.33 (26%)	27.81

Table 6. Annual deposition (kg ha^{-1} yr^{-1}) of wet-only, dry-only and wet+dry deposition for two different sampling periods: 1) 2002-2003, and 2) April 2009-July 2010. Percentages relative to total (wet+dry) are also indicated.

Annual deposition (kg ha^{-1} yr^{-1})	2002-2003 (Castillo 2006)			April 2009 - July 2010 (this study)		
	Wet-only	Dry-only	Wet+dry	Wet-only	Dry-only	Wet+dry
Na^+	4,98 (86%)	0,83 (14%)	5,81	2,07 (76%)	0,64 (24%)	2,71
K^+	1,19 (58%)	0,87 (42%)	2,06	0,87 (54%)	0,76 (46%)	1,63
Ca^{2+}	9,74 (59%)	6,76 (41%)	16,50	4,92 (60%)	3,26 (40%)	8,18
Mg^{2+}	0,98 (67%)	0,48 (33%)	1,46	0,49 (65%)	0,27 (35%)	0,76
$N\text{-}NH_4^+$	3,36 (82%)	0,73 (18%)	4,09	3,71 (95%)	0,18 (5%)	3,90
$N\text{-}NO_3^-$	2,88 (78%)	0,79 (22%)	3,67	2,42 (79%)	0,62 (21%)	3,04
$S\text{-}SO_4^{2-}$	4,78 (84%)	0,9 (16%)	5,68	2,48 (82%)	0,55 (18%)	3,03
Cl^-	8,64 (84%)	1,61 (16%)	10,25	3,52 (77%)	1,05 (23%)	4,57
Total	36,5 (74%)	13.0(26%)	49,5	20,5 (74%)	7,33 (26%)	27,8

Figure captions

Figure 1. Map of Montseny study site, northeastern Spain.

Figure 2. Atmospheric deposition sampling and precipitation measurement at LC station: a) open bulk deposition collectors; b) Andersen wet/dry sampler (ESM Andersen instruments. G78-1001).

Figure 3. Spearman rank correlations (ρ) between the analyzed ions in: a) bulk, b) wet and c) dry deposition.

Figure 4. Comparison of wet+dry and bulk+DAR deposition (in kg ha^{-1} yr^{-1}) for each chemical species in Montseny.

Figure 1

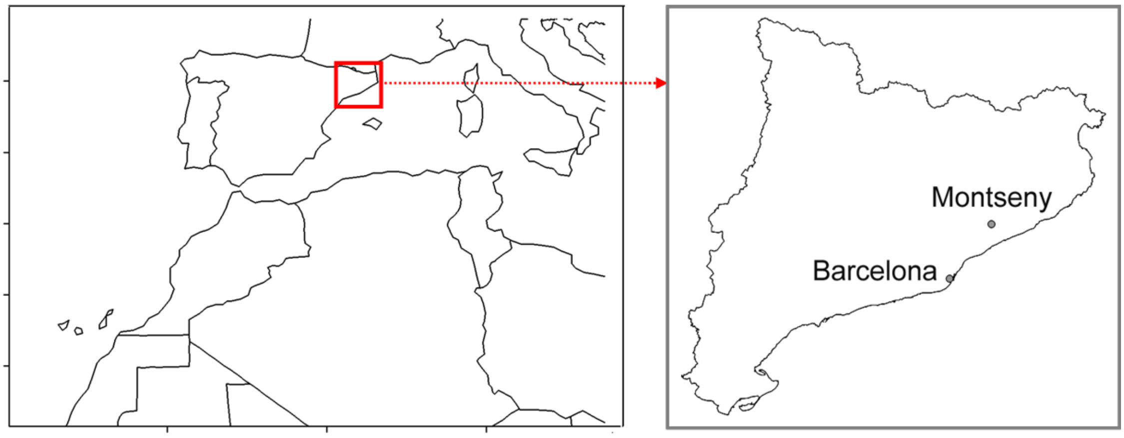


Figure 2

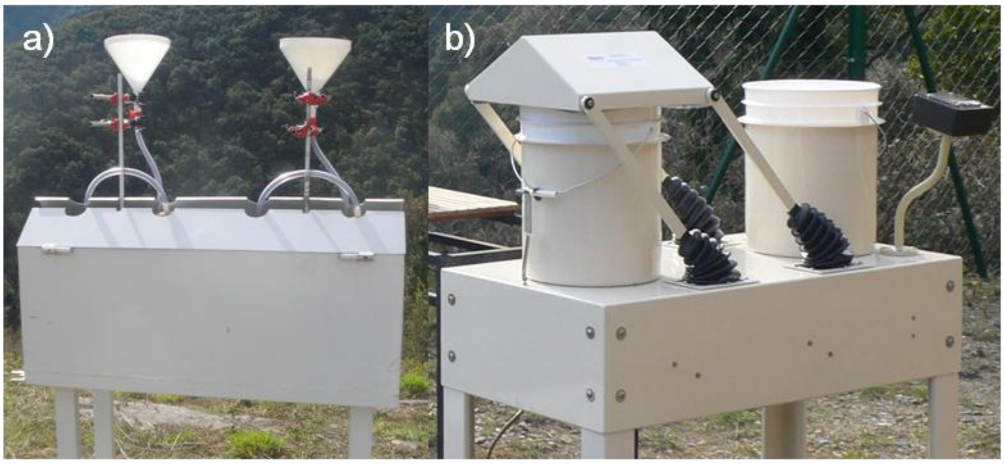


Figure 3

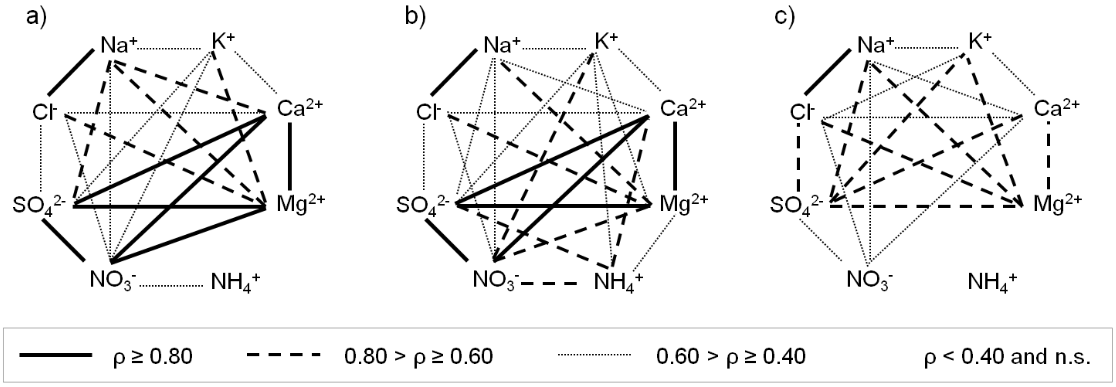
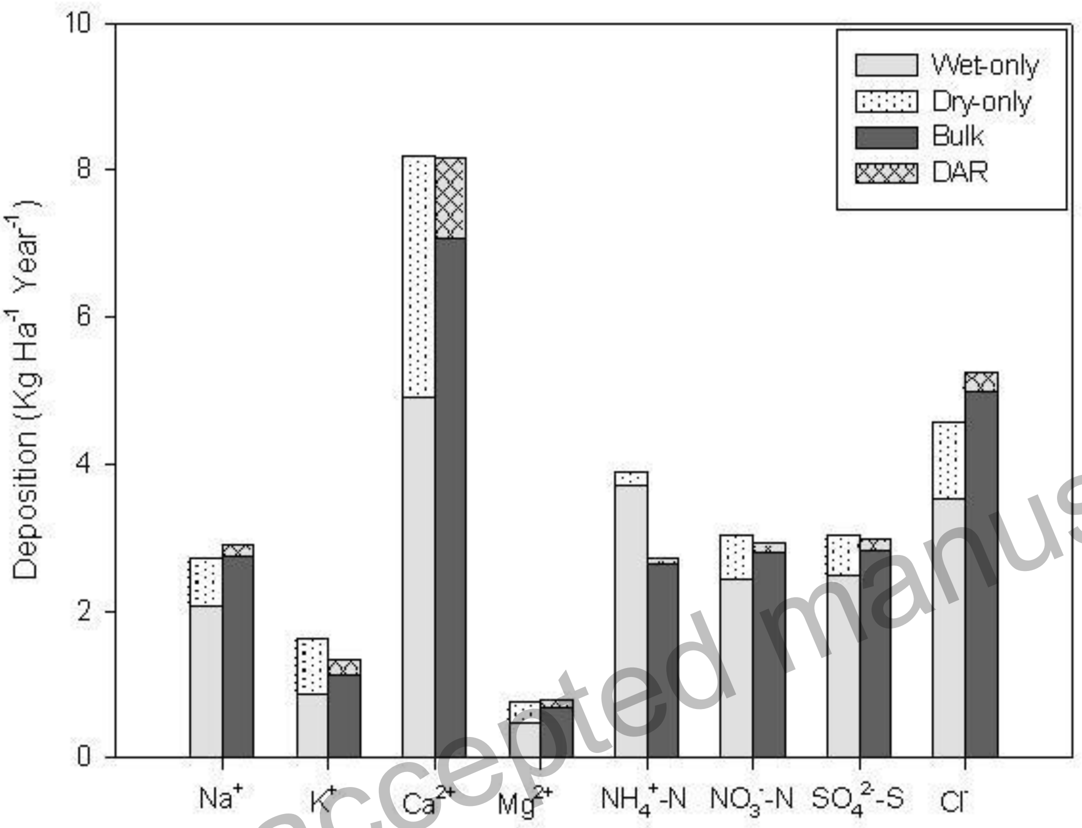

a)
b)
c)
Na^+
K^+
Cl^-
Ca^{2+}
SO_4^{2-}
Mg^{2+}
NO_3^-
NH_4^+
$\rho \geq 0.80$
$0.80 > \rho \geq 0.60$
$0.60 > \rho \geq 0.40$
$\rho < 0.40$ and n.s.

Figure 4


10
8
6
4
2
0
Deposition (Kg Ha^{-1} Year^{-1})
Wet-only
Dry-only
Bulk
DAR
Na$^+$
K$^+$
Ca^{2+}
Mg^{2+}
NH$_4^+$-N
NO$_3^-$-N
SO$_4^{2-}$-S
Cl$^-$