

## A comparison of bulk and wet-only deposition at two adjacent sites in Melle (Belgium)

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### Abstract

During 9 months, the weekly bulk and wet-only precipitation depositions in an urbanised region of Flanders (Belgium) were compared at two sites with a different height and separated by 1 km. The amount of rainfall at the two sites was similar, and the difference in ion deposition between the two sites was generally less than 5%. While the amount of rainfall measured was almost the same for both collector types, bulk deposition was significantly ( $p < 0.02$ ) higher than the wet deposition of all ions other than  $H^+$  and  $NH_4^+$ . Averaged for both sites, bulk deposition was 129% ( $K^+$ ), 84% ( $Ca^{2+}$ ), 51% ( $Cl^-$ ), 50% ( $Mg^{2+}$ ), 46% ( $Na^+$ ), 32% ( $SO_4^{2-}$ ), 27% ( $NO_3^-$ ), 17% ( $F^-$ ), and 11% ( $NH_4^+$ ) higher than wet-only deposition. The acidity of bulk samples was significantly ( $p < 0.06$ ) lower than the acidity of wet-only samples. Bulk  $NH_4^+$  concentrations were only significantly ( $p < 0.002$ ) higher than wet-only concentrations at one site because of the sensor-related, delayed closing of the wet-only lid at the second site. Although dry deposition significantly contributed to bulk precipitation measurements, bulk deposition exceeded the wet acidifying deposition of  $NO_3^-$ ,  $NH_4^+$ , and  $SO_4^{2-}$  by less than 25%.

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### 1. Introduction

Atmospheric deposition contributes to the chemistry of plants, soils, and surface waters, and to the cycling of nutrients in ecosystems (Richter and Lindberg, 1988). Therefore, the accurate quantification of wet, dry and occult deposition is important for a wide range of ecological disciplines. Wet deposition is defined as the

process by which atmospheric compounds are attached to and dissolved in cloud and precipitation droplets and delivered to the earth's surface by rain, hail or snow (Draaijers et al., 1998). In theory, wet deposition is best measured using wet-only samplers, which are covered by a lid during dry periods and open whenever precipitation is detected by a sensor. As wet-only collectors have the drawback of being expensive and requiring a power supply, continuously open funnels or bulk collectors are often used to collect precipitation in ecological studies.

Differences in the chemical composition of precipitation collected by wet-only and bulk collectors have been

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assessed in a number of comparative studies (Table 1), and average correction factors for the contribution of dry deposition onto the funnels have been derived from parallel measurements. However, the amount of dry deposition onto bulk precipitation collectors depends on local gas and aerosol concentrations, turbulence intensities and the collection efficiency of the samplers (Draaijers et al., 1998). Calcium, magnesium and potassium concentrations are often higher in bulk samples than in wet-only samples, because of the deposition of soil-derived particles on the walls of the collectors during dry periods (Thimonier, 1998). Differences for nitrate, ammonium, and sulphate are usually smaller, but local or regional sources of emissions can significantly influence the composition of bulk samples (Stedman et al., 1990).

If bulk samplers are used to quantify precipitation chemistry, short-term parallel wet-only and bulk measurements are recommended to estimate site-specific correction factors for the contribution of dry deposition onto funnels (Draaijers et al., 1998). To our knowledge, no comparison between bulk and wet-only deposition has been made for Flanders. However, acidifying deposition in the north of Belgium is known to be among the highest in Europe (UNECE and EC, 2003), and it is hypothesised that dry deposition accounts for

40–55% of the atmospheric sulphur deposition and 50–80% of the nitrogen deposition on forest and heather vegetation in Flanders (VMM, 2002). Bulk precipitation is sampled in the framework of the Pan-European Intensive Monitoring Programme of EU/ICP Forest and the data are, for example, used to model the dry deposition of inorganic nitrogen onto forest canopies. Precipitation is normally measured at a site in the open field located in the vicinity of the studied forest stand, instead of the rainfall being measured above the forest canopy. The aims of the study were therefore: (i) to assess the systematic bias on precipitation chemistry measured by using continuously open funnel collectors, and (ii) to compare the precipitation chemistry measured at different heights at two sites separated by 1 km.

## 2. Experimental

### 2.1. Study site and meteorological conditions

Both bulk and wet-only precipitation were measured at two neighbouring sites (Fig. 1) in Melle (50°58'N, 3°49'E, 16 m a.s.l.) in the north of Belgium, ca. 60 km from the North Sea. Average precipitation between 1980 and 2002 was 755 mm y<sup>-1</sup> and mean annual temperature

Table 1

Ratio of volume-weighted mean bulk and wet-only concentrations in precipitation, as measured at several locations throughout the world: reference, sampling interval (SI), and bulk over wet-only ratio per ion

Location	Reference	SI <sup>a</sup>	H <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	NH <sub>4</sub> <sup>+</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>
Leadville, USA	Ranalli et al. (1997)	w	0.65	2.03	1.67	1.64	2.55	1.26	1.29	1.51	1.57
Oak Ridge, USA	Richter and Lindberg (1988)	5-w	<i>1.04</i>	—	4.41	2.44	—	—	0.68	1.15	—
Hong Kong, China	Tanner (1999)	d	0.86	1.03	1.09	1.57	1.06	—	<i>0.99</i>	<i>1.01</i>	<i>1.01</i>
Kobe, Japan	Aikawa et al. (2003)	w	0.29	—	—	3.96 <sup>b</sup>	—	1.56	1.84	1.48 <sup>b</sup>	—
Toyo-oka, Japan	Aikawa et al. (2003)	w	0.53	—	—	<i>1.73<sup>b</sup></i>	—	1.36	1.19	1.16 <sup>b</sup>	—
Kaibara, Japan	Aikawa et al. (2003)	w	0.79	—	—	<i>1.87<sup>b</sup></i>	—	<i>1.24</i>	<i>1.20</i>	<i>1.19<sup>b</sup></i>	—
Delhi, India	Kulshrestha et al. (1995)	d	0.63 <sup>c</sup>	1.01 <sup>c</sup>	1.30 <sup>c</sup>	2.03 <sup>c</sup>	2.06 <sup>c</sup>	0.93 <sup>c</sup>	1.08 <sup>c</sup>	1.02 <sup>c</sup>	1.16 <sup>c</sup>
Istanbul, Turkey	Akkoyunlu and Tayanc (2003)	w	0.52 <sup>d</sup>	1.63 <sup>d</sup>	2.82 <sup>d</sup>	2.60 <sup>d</sup>	2.15 <sup>d</sup>	1.36 <sup>d</sup>	1.26 <sup>d</sup>	4.39 <sup>d</sup>	1.64 <sup>d</sup>
Pallanza, Italy	Mosello et al. (1988)	w	0.98	1.10	1.50	1.32	1.29	1.06	1.12	1.08	1.08
Manchester, UK	Lee and Longhurst (1992)	w	0.50	—	—	1.87	—	<i>1.21</i>	<i>1.17</i>	1.18	—
Eskdalemuir, UK	Stedman et al. (1990)	w	<i>1.00</i>	0.97	<i>0.89</i>	1.14	<i>0.90</i>	0.87	<i>1.00</i>	<i>0.98</i>	0.93
Stoke Ferry, UK	Stedman et al. (1990)	w	1.28	1.41	<i>1.00</i>	1.45	1.42	0.84	<i>1.10</i>	<i>1.05</i>	1.39
Ludlow, UK	Stedman et al. (1990)	w	<i>1.09</i>	1.93	<i>1.33</i>	1.86	1.88	<i>1.12</i>	1.36	1.23	1.88
Lough Navar, UK	Stedman et al. (1990)	w	<i>0.83</i>	<i>0.99</i>	<i>0.94</i>	<i>1.18</i>	<i>0.99</i>	0.60	<i>0.85</i>	<i>0.94</i>	<i>1.01</i>
Barcombe Mills, UK	Stedman et al. (1990)	w	1.22	1.35	<i>1.53</i>	1.76	1.29	<i>1.00</i>	1.30	1.36	1.33
Yarner Wood, UK	Stedman et al. (1990)	w	<i>1.07</i>	<i>0.85</i>	<i>0.85</i>	<i>1.05</i>	<i>0.83</i>	0.72	<i>1.00</i>	<i>0.95</i>	<i>0.84</i>
High Muffles, UK	Stedman et al. (1990)	w	<i>0.97</i>	<i>1.14</i>	<i>1.22</i>	1.37	1.13	0.92	<i>1.04</i>	<i>0.99</i>	1.10
Strathvaich Dam, UK	Stedman et al. (1990)	w	<i>1.23</i>	1.29	<i>1.00</i>	<i>0.73</i>	1.17	0.55	0.92	<i>1.03</i>	1.29
Glen Dye, UK	Stedman et al. (1990)	w	<i>1.02</i>	1.38	<i>1.22</i>	1.16	1.29	0.88	<i>0.98</i>	<i>1.01</i>	1.29
Ghent, Belgium	Present study	w	0.37	1.46	2.28	1.84	1.50	<i>1.11</i>	1.27	1.32	1.51

Values in italic indicate a non-significant ( $p > 0.05$ ) difference between bulk and wet-only ion concentration.

<sup>a</sup>Sampling interval of bulk precipitation measurements: d: daily, w: weekly.

<sup>b</sup>Non-marine fraction.

<sup>c</sup>Significance of the difference between bulk and wet-only concentrations was not tested.

<sup>d</sup>Ratio of arithmetic mean concentration of bulk and wet-only precipitation.

was 10.2 °C (data of the Royal Meteorological Institute of Belgium). Regional land use is a mixture of arable land and urban zones. At one site (site T), precipitation was collected on top of a 35-m-high tower located in a mixed deciduous forest of 30 ha with a mean tree height of 27 m. The shortest distance from the tower to the forest edge is 60 m (Fig. 1). A cattle farm is located next to the forest.

The second site (site F) was located in the open field, on grass vegetation surrounded by meadows and arable land. One of the main motorways in Belgium is situated at a distance of about 250 m from the site (Fig. 1). Site F is a meteorological station of the Royal Meteorological Society of Belgium, and the amount of precipitation is measured at 10-min intervals by a tipping bucket gauge. The chemical composition of bulk precipitation at site F has been measured since 1992, within the framework of the UNECE Forest Monitoring Programme.

During 11 of the 40 measured weeks, the amount of weekly precipitation measured was less than 1 mm

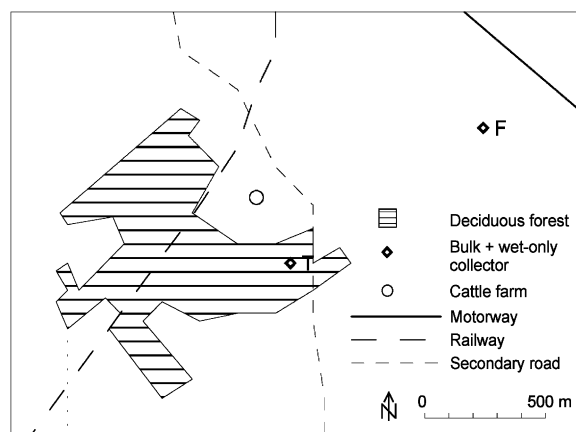


Fig. 1. Location of the tower (T) and field (F) site in Melle, Belgium.

(Fig. 2). No snowfall occurred during the study period. Weekly average wind velocities at site F ranged from 1.7 to 4.6  $\text{m s}^{-1}$ . The main wind direction was southwest.

## 2.2. Data collection

The quantity and chemistry of wet-only and bulk precipitation were measured weekly from 4 March to 9 December 2003. Wet-only precipitation was collected by automatic wet-only samplers (Eigenbrodt) with an orifice diameter of 25.4 cm, set at a height of 1.9 m. For site T, the actual height of the collecting surface was 36.9 m above ground level. Rainfall sensors with a delay time of 1 s activated the opening of the lid. An electrical, resistance-driven rain sensor (RS 85, Eigenbrodt) was used at site T and an optical sensor (IRSS 88, Eigenbrodt) at site F. Rainwater was stored in 5-l glass bottles that were refrigerated at a temperature of 4 °C. All parts of the collector that came into contact with rainwater were made of teflon, and were cleaned once every 2 weeks using demineralised water. The reproducibility of the wet-only sampling system has been tested thoroughly by means of paired measurements (VMM, 2002).

Bulk precipitation was collected using polyethylene funnels with a diameter of 24.2 cm, a sharp-edged vertical rim and a slope of 45°, set at a height of 1.5 m above ground level (36.5 m above ground level for site T). Two bulk precipitation collectors were used at site T and four bulk precipitation collectors at site F. A nylon wire mesh placed in the funnels prevented contamination by large particles. Funnels were supported by and drained into 2-l polyethylene bottles. At site F, collecting bottles were placed below ground level to avoid the growth of algae and to keep the samples cool. As placing below ground level was not possible at site T, bottles were wrapped in aluminium foil. Funnels, wire meshes, and bottles were replaced weekly with equipment that had been cleaned using demineralised water.

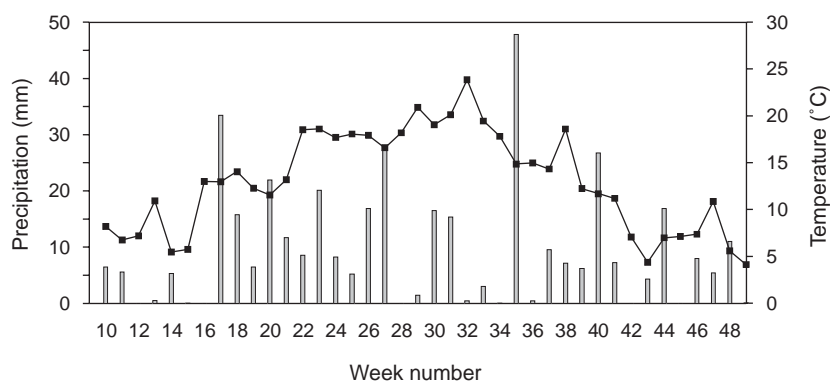


Fig. 2. Weekly precipitation (mm) and mean temperature (°C) at the field site.

At both sites two passive samplers (Palme tubes, Gradko, UK) were exposed in an open box to adsorb atmospheric ammonia during 4-week sampling periods. The passive samplers were at a height of 36.5 m above ground level at site T, and 2 m above ground level at site F. The passive samplers adsorb  $\text{NH}_3$  as  $\text{NH}_4^+$  by phosphoric acid. Atmospheric  $\text{NH}_4^+$  salts are not adsorbed since they cannot penetrate the sampler wall (Swaans and Aerts, 2004).

### 2.3. Chemical analysis and data quality

Rain samples were kept cool during transport, and stored in darkness at 4 °C in the laboratory. Water pH (pH meter CG841, Schott) and conductivity (Konduktometer CG855, Schott) were measured within 1 week after sampling. Anions ( $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ) and cations ( $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$ ) were determined using ion chromatography (Dionex DX300 and DX120) according to the ISO-10304 standard within 1 month after sampling. Ion chromatograph samples passed a 20 and 5  $\mu\text{m}$  in-line filter (Dionex) before analysis.  $\text{H}^+$  concentrations were derived from pH measurements. Determination limits (DL,  $\mu\text{eq l}^{-1}$ ) of the chemical analyses were 5.7 ( $\text{Na}^+$ ), 1.8 ( $\text{K}^+$ ), 11 ( $\text{Ca}^{2+}$ ), 1.7 ( $\text{Mg}^{2+}$ ), 1.7 ( $\text{NH}_4^+$ ), 1.0 ( $\text{NO}_3^-$ ), 1.0 ( $\text{Cl}^-$ ), 2.9 ( $\text{SO}_4^{2-}$ ), 9.1 ( $\text{PO}_4^{3-}$ ), 1.6 ( $\text{F}^-$ ), and 1.1 ( $\text{NO}_2^-$ ). The accuracy of the analyses was evaluated by checking the ion balance ( $< 0.2 \mu\text{eq l}^{-1}$ ) and by comparing the measured and calculated conductivity of water samples. Phosphate concentration was below the DL in all measured rain samples, indicating that samples were not contaminated by bird droppings (Erisman et al., 2003). Nitrite was below the DL in about 50% of the samples, and therefore the  $\text{NO}_2^-$  results have not been used. On the few occasions that  $\text{K}^+$  and  $\text{F}^-$  concentrations were below the DL, the concentrations were assumed to be equal to half of the DL.

Within 1 week after exposure, the passive  $\text{NH}_3$  samplers were desorbed with 10 ml ultrapure water, which was then analysed using spectrophotometry. For each sampling period two blank samplers were analysed. The average  $\text{NH}_3$  concentration ( $\mu\text{g m}^{-3}$ ) in each sampling period was calculated using an experimentally determined sampling rate of  $3.9 \text{ m}^3 \text{ s}^{-1}$  (Swaans and Aerts, 2004). The relative standard deviation between the two samplers for each site and sampling period was generally below 5%. No correction was made for temperature or relative humidity.

### 2.4. Data analysis

Three methods were used to compare the weekly rainfall amounts and ion concentrations between collector types and sites. First, scatter plots of wet-only against bulk concentration measurements for each ion

were visually inspected for both sites. Second, Wilcoxon signed rank tests were performed to test whether weekly rainfall amounts and ion concentrations were significantly different between collector types. This non-parametric test was used because according to the Shapiro–Wilk test ( $p < 0.05$ ), the differences between wet-only and bulk precipitation variables did not approximate a normal distribution. Third, mean ion concentrations in bulk and wet-only samples were calculated as precipitation volume-weighted (vw) means, so as to account for the effect of precipitation amount on ion concentrations.

Pearson correlation coefficients were calculated between the variables in the wet-only data and the bulk data of both study sites together. The role of  $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  in neutralizing rainwater acidity was validated by calculating neutralization factors as the ratio of the equivalent concentration of each ion to the sum of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  concentrations (Kulshrestha et al., 1995). Non-marine  $\text{SO}_4^{2-}$  deposition was calculated using an equivalent  $\text{SO}_4^{2-}/\text{Na}^+$  seawater ratio of 0.12 (Stedman et al., 1990; VMM, 2002), assuming that all deposited  $\text{Na}^+$  originates from seawater. A paired samples *t*-test was used to compare the atmospheric  $\text{NH}_3$  concentrations between both sites because according to the Shapiro–Wilk test ( $p = 0.92$ ), the concentration difference between sites approximated a normal distribution. All statistical analyses were performed using SPSS for Windows version 11.0.

## 3. Results

### 3.1. Comparison of sites

Almost the same rainfall amounts were measured at both study sites (Table 2). Wilcoxon signed rank tests revealed no statistically significant differences. Over the study period, the cumulative rainfall at site F was 0.7% higher for the wet-only samplers ( $p = 0.76$ ) and 1.7% higher for the bulk samplers ( $p = 0.21$ ) compared to site T. At site F, the wet-only rainfall was 2.1% lower and the bulk rainfall 1.4% lower than the measurements of the Royal Meteorological Institute of Belgium.

The composition of rainfall was similar at both sites (Table 2). Volume-weighted (vw) mean ion concentration generally differed by less than 5% between the two sites and always by less than 10%, except for  $\text{H}^+$ . For the wet-only samples, vw mean  $\text{H}^+$  concentration was 35% lower at site T than at site F, whereas the bulk  $\text{H}^+$  concentration was on average 35% higher at site T. According to the Wilcoxon tests, weekly wet-only concentrations of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  were significantly ( $p < 0.05$ ) higher at site T than at site F. Bulk  $\text{NH}_4^+$  concentration was lower at site T, but not significantly ( $p = 0.441$ ). Finally, bulk rainfall concentrations

Table 2

Bulk and wet-only precipitation at two adjacent sampling sites: amount (mm) and volume-weighted (vw) mean pH (–) and ion concentrations ( $\mu\text{eq l}^{-1}$ ), ratio of the vw mean bulk and wet-only concentrations, and significance of the difference between bulk and wet-only concentrations (Wilcoxon signed rank test)

	Site T (tower)				Site F (field)			
	Wet	Bulk	Ratio	Sign.	Wet	Bulk	Ratio	Sign.
Water	382.1	381.2	1.00	0.310	384.8	387.7	1.01	0.765
pH <sup>a</sup>	5.19	5.45	—	0.082	5.00	5.58	—	0.002
H <sup>+</sup>	6.51	3.55	0.54	0.061	10.08	2.61	0.26	0.001
Na <sup>+</sup>	36.98	56.04	1.52	<0.001	37.49	52.83	1.41	0.016
K <sup>+</sup>	1.96	4.27	2.18	<0.001	1.93	4.61	2.39	<0.001
Ca <sup>2+</sup>	26.87	48.90	1.82	<0.001	25.06	46.59	1.86	<0.001
Mg <sup>2+</sup>	9.25	14.32	1.55	<0.001	9.43	13.65	1.45	<0.001
NH <sub>4</sub> <sup>+</sup>	65.65	68.98	1.05	0.370	62.16	72.93	1.17	0.002
NO <sub>3</sub> <sup>-</sup>	31.26	39.77	1.27	<0.001	30.62	38.81	1.27	<0.001
Cl <sup>-</sup>	33.37	51.99	1.56	<0.001	33.70	49.06	1.46	<0.001
SO <sub>4</sub> <sup>2-</sup>	47.32	61.47	1.30	<0.001	44.79	59.68	1.33	<0.001
F <sup>-</sup>	1.59	2.15	1.35	<0.001	1.48	1.97	1.32	<0.001

<sup>a</sup>pH-values were calculated as the negative logarithm of the corresponding mean vw H<sup>+</sup> concentrations.

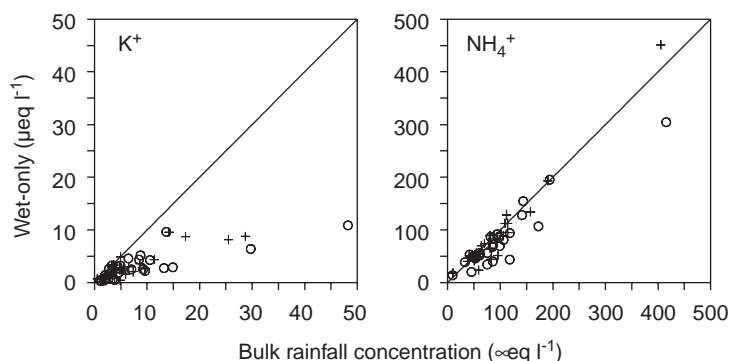


Fig. 3. Weekly wet-only and bulk rainfall concentrations ( $\mu\text{eq l}^{-1}$ ) of K<sup>+</sup> and NH<sub>4</sub><sup>+</sup> at the tower site (+) and the field site (O).

differed significantly ( $p < 0.05$ ) between sites for H<sup>+</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, and F<sup>-</sup>.

### 3.2. Comparison of sampling devices

Almost the same rainfall amounts were measured for both collector types (Table 2). Over the study period, the wet-only sampler collected 0.2% more precipitation than the bulk sampler at site T ( $p = 0.31$ ), and 0.7% less than the bulk sampler at site F ( $p = 0.72$ ).

According to the Wilcoxon signed rank tests, weekly bulk rainfall concentrations were significantly ( $p < 0.02$ ) higher than wet-only concentrations for all ions, except for NH<sub>4</sub><sup>+</sup> and H<sup>+</sup> (Table 2). Although the NH<sub>4</sub><sup>+</sup> concentrations were higher in bulk rainfall than in wet-only rainfall at both sites, the difference between both collector types was only significant ( $p = 0.002$ ) at

site F (Fig. 3). In contrast to all other ions, H<sup>+</sup> concentrations were significantly ( $p < 0.06$ ) lower in bulk rainfall than in wet-only rainfall.

The calculated volume-weighted (vw) mean ion concentrations were higher in bulk rainfall than in wet-only rainfall for all ions except H<sup>+</sup>, in agreement with the Wilcoxon tests. The greatest difference was found for K<sup>+</sup>, for which the vw mean bulk concentration was 2.2 times higher than the wet-only concentration at site T, and 2.4 times higher at site F (Table 2). Arranged according to decreasing concentration ratios of bulk over wet-only rainfall, the ion order was K<sup>+</sup>, Ca<sup>2+</sup>, Cl<sup>-</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, SO<sub>4</sub><sup>2+</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, and H<sup>+</sup>.

High and significant ( $p < 0.001$ ,  $n = 58$ ) Pearson correlations were found in wet-only and bulk precipitation between Na<sup>+</sup> and Cl<sup>-</sup> ( $r > 0.97$ ), and between NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup> ( $r > 0.92$ ). Ca<sup>2+</sup> was more

strongly correlated with  $K^+$  ( $r = 0.92$ ) and  $SO_4^{2-}$  ( $r = 0.95$ ) in the bulk precipitation than in the wet-only precipitation ( $r = 0.65$  and  $0.85$ , respectively).  $Mg^{2+}$ , on the other hand, was more strongly correlated with  $Na^+$  ( $r = 0.97$ ) and  $Cl^-$  ( $r = 0.97$ ) in the wet-only precipitation than in the bulk precipitation ( $r = 0.82$  and  $0.82$ , respectively). All variables were significantly ( $p < 0.05$ ) negatively correlated with the amount of precipitation, except for pH and  $H^+$ , and  $Cl^-$  in the wet-only data, for which no significant correlations were found. The values of the neutralization factor for  $NH_4^+$ ,  $Ca^{2+}$ , and  $Mg^{2+}$  were, respectively, 0.83, 0.34, and 0.12 for the wet-only samples and 0.71, 0.48, and 0.14 for the bulk samples.

### 3.3. Atmospheric $NH_3$ concentrations

The average  $NH_3$  concentration measured by the passive samplers over the study period was  $5.58 \mu g m^{-3}$  at site T, which was significantly lower ( $p = 0.031$ ) than the  $NH_3$  concentration of  $6.17 \mu g m^{-3}$  at site F. There was a seasonal variation in atmospheric  $NH_3$  concentrations, with peaks in March and August (Fig. 4).

### 3.4. Wet and bulk precipitation deposition

Since the measured precipitation amount was almost equal for both collector types, the bulk/wet-only deposition ratios equal the bulk/wet-only vw mean concentration ratios (Table 2). Averaged for both sites, bulk deposition was 129% ( $K^+$ ), 84% ( $Ca^{2+}$ ), 51% ( $Cl^-$ ), 50% ( $Mg^{2+}$ ), 46% ( $Na^+$ ), 32% ( $SO_4^{2-}$ ), 27% ( $NO_3^-$ ), 17% ( $F^-$ ), and 11% ( $NH_4^+$ ) higher than wet-only deposition, while bulk  $H^+$  was 60% lower. Over the 9-month study period, the wet acidifying deposition of  $SO_4^{2-}$ ,  $NO_3^-$ , and  $NH_4^+$  was  $55.1 \mu eq m^{-2}$  at site T and  $52.9 \mu eq m^{-2}$  at site F. The bulk acidifying deposition was  $64.9 \mu eq m^{-2}$  at site T and  $66.5 \mu eq m^{-2}$  at site F. This calculation of the deposition of potential acidity

takes into account the microbial transformation of ammonium to nitrate with the resultant release of a hydrogen ion.

## 4. Discussion

### 4.1. Rainfall amount

The collection efficiency of a precipitation sampler is determined by the disturbance of the airflow over and around the collector, height above the ground, evaporation of collected rainwater, and, in the case of a wet-only collector, the efficiency of the rain sensor (Stedman et al., 1990). In general, wet-only devices are reported to collect less precipitation than other samplers, which is commonly attributed to their higher aerodynamic blockage. In the United Kingdom, for example, the collection efficiency of nine wet-only collectors relative to bulk collectors ranged from 71% to 92% and generally decreased with increasing wind speed at the site (Stedman et al., 1990). Yet, in the present study, the total amount of rainfall collected by bulk and wet-only devices differed by less than 1%. This might be due to the relatively low wind speeds at the sites. With respect to sensor sensitivity, no delayed opening of the wet-only lid was observed in the field, even at low rainfall intensities.

### 4.2. Deposition of $Na^+$ , $K^+$ , $Ca^{2+}$ , $Mg^{2+}$ , and $Cl^-$

The greatest difference between bulk and wet-only precipitation collectors was found for the base cations and  $Cl^-$ , with mean concentration ratios of bulk/wet-only rainfall of 2.3 for  $K^+$ , 1.8 for  $Ca^{2+}$ , and 1.5 for  $Mg^{2+}$ ,  $Na^+$ , and  $Cl^-$ . Therefore during the study period, dry deposition of sedimenting particles onto the bulk samplers contributed between 50% and 130% of

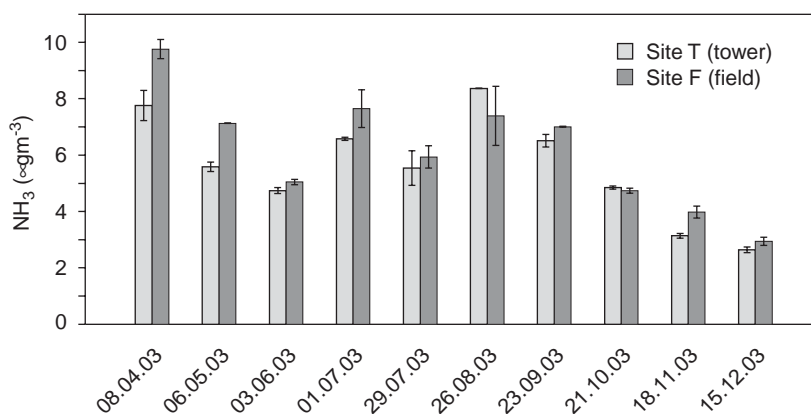


Fig. 4. Atmospheric  $NH_3$  concentration measured by passive samplers during 4 weekly periods at two adjacent sites. The error bars indicate standard deviations.

the bulk deposition of base cations and  $\text{Cl}^-$ , depending on the ion. These findings correspond well to previously reported research (Table 1). However, it should be noted that a considerable variation in bulk/wet-only ratios has been observed, depending on sampler type, location, meteorological circumstances, and sampling interval. The variability in bulk/wet-only ratios is usually smaller between ions than between locations, which suggests that the dry deposition rate of cations is influenced more by local circumstances than by the ion concerned. Similarly, in a Canadian study (Houle et al., 1999), regression analyses suggested that the wet/dry ratio of  $\text{Na}^+$  was the same for the other base cations.

The high correlation between  $\text{Cl}^-$  and  $\text{Na}^+$  or  $\text{Mg}^{2+}$  in the precipitation indicates a common source, i.e. marine.  $\text{Ca}^{2+}$  and  $\text{K}^+$  had a stronger correlation in bulk than in wet-only samples, which confirms that both cations readily undergo dry deposition and mainly originate from the same source, i.e. soil particles (Akkoyunlu and Tayanç, 2003). No difference between base cation depositions was found between sites at a different height. This is in contrast to Kulshrestha et al. (1995), who found that the vw mean  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations in India were 122% and 68% higher for bulk collectors at a height of 13 m than at a height of 30 m.

#### 4.3. Deposition of $\text{NH}_4^+$ , $\text{NO}_3^-$ , $\text{SO}_4^{2-}$ , $\text{F}^-$ , and $\text{H}^+$

Bulk deposition of  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{F}^-$  was 30% higher ( $p < 0.001$ ) than wet-only deposition, while the bulk  $\text{H}^+$  deposition was significantly ( $p < 0.06$ ) lower than the wet-only deposition. Although the measured atmospheric  $\text{NH}_3$  concentrations were relatively high (Walker et al., 2004), almost all  $\text{NH}_4^+$  collected by bulk samplers was the result of wet deposition.

The most pronounced differences between sites were found for  $\text{NH}_4^+$  and  $\text{H}^+$ . Scatter plots showed that the weekly bulk concentration of  $\text{NH}_4^+$  was higher than the wet-only concentration at both sites (Fig. 3, Table 2). However, the difference between bulk and wet-only  $\text{NH}_4^+$  concentration was only significant ( $p = 0.002$ ) at the field site, due to the significantly ( $p < 0.05$ ) lower wet-only deposition and the higher bulk deposition at the field site compared to the tower site. The higher bulk  $\text{NH}_4^+$  deposition at the field site suggests a higher dry deposition of  $\text{NH}_4^+$  onto bulk funnels (Table 2). This is in line with the significantly ( $p < 0.05$ ) higher atmospheric  $\text{NH}_3$  concentrations at the field site, which is surrounded by manured fields. The significantly higher wet-only  $\text{NH}_4^+$  deposition at the tower site than at the field site was most probably due to different rainfall sensors being used at the two sites. While the optically driven, wet-only lid at the field site was closed immediately after rain events, the electrical, resistance-driven wet-only lid at the tower site was

opened for much longer, until 15 min after rain events. As the highest dry deposition rates of  $\text{NH}_3$  (Cape and Leith, 2002) and particles (Ruijgrok et al., 1997) are obtained for wet surfaces, this longer opening time probably resulted in a higher dry deposition of  $\text{NH}_3$  and  $\text{NH}_4^+$  particles onto the wet-only collector after rain events. Mean wet-only concentrations of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  were also higher at the tower site than at the field site.

Cape and Leith (2002) experimentally found that the amount of  $\text{SO}_2$  deposited on wet funnel surfaces was closely related to the amount of  $\text{NH}_3$  deposited. This was mainly attributed to the oxidation of dissolved  $\text{SO}_2$ , which retains dissolved  $\text{NH}_3$  as involatile  $(\text{NH}_4)_2\text{SO}_4$  salts as the water evaporates. Co-deposition of  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  is also suggested in the present study by the high correlation between the concentration of these ions in bulk and wet deposition. However, other  $\text{SO}_4^{2-}$ -containing salts than  $(\text{NH}_4)_2\text{SO}_4$  may be deposited on funnel surfaces (Cape and Leith, 2002), which explains why the measured bulk/wet-only ratios were higher for  $\text{SO}_4^{2-}$  than for  $\text{NH}_4^+$ .  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$  mainly originate from anthropogenic sources (Tanner, 1999). Assuming that all deposited  $\text{Na}^+$  originates from seawater, non-marine  $\text{SO}_4^{2-}$  contributed 90% of wet  $\text{SO}_4^{2-}$  deposition.

The acidity of a rainwater sample is determined by the balance of the anions and other cations present. This is clearly demonstrated by plotting pH as a function of the ratio of  $(\text{NH}_4 + \text{Ca} + \text{Mg})$  to  $(\text{SO}_4 + \text{NO}_3)$  (Fig. 5). The calculated neutralization factors indicate that  $\text{NH}_4^+$  was the main acid-neutralizing ion. Therefore, the difference in  $\text{NH}_4^+$  concentration between sites for similar collecting devices explains most of the difference in  $\text{H}^+$  concentration between sites. The hydrogen concentrations in bulk rainfall were significantly

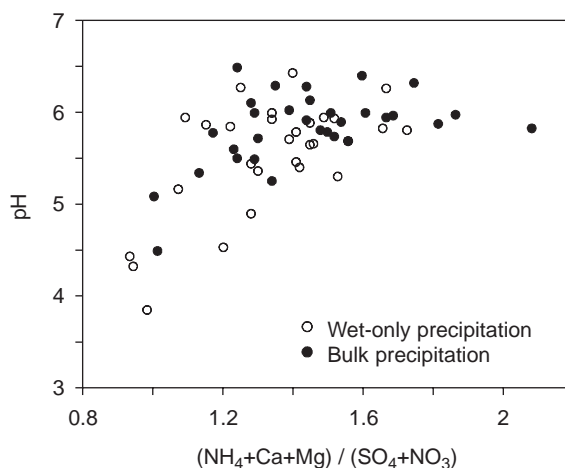


Fig. 5. The pH of wet-only and bulk precipitation at the field site in relation to the ratio of equivalent  $(\text{NH}_4 + \text{Ca} + \text{Mg}) / (\text{SO}_4 + \text{NO}_3)$  concentrations.

( $p < 0.06$ ) lower than in wet-only rainfall. The neutralization factors show that the lower  $H^+$  concentrations in the bulk rainfall compared to the wet-only rainfall were mainly due to the extra reduction of acidity by dry deposited  $Ca^{2+}$  compounds (Lee and Longhurst, 1992).

#### 4.4. Impact of rainfall distribution on precipitation deposition

The year 2003 was exceptionally dry. During the 9-month period only 382 mm precipitation was collected, which is only 63% of the average 1980–2002 amount of 606 mm for this period and location. The low precipitation amount explains why the wet ion deposition was relatively low compared to other years. Dry-deposition fluxes can vary considerably, depending on the nature and position of the receptor surfaces, and the meteorological conditions. Dry deposition of bulk funnels depends on how long and how often funnel surfaces are wetted (Cape and Leith, 2002). Therefore, the occurrence of 25% of dry weeks combined with the weekly replacement of bulk samplers by clean equipment has almost certainly resulted in an underestimation of the dry deposition on bulk funnels. In other words, the bulk/wet-only ratios presented are conservative estimates, and in years with higher precipitation amounts, the systematic bias on precipitation composition measured by bulk funnels could be higher.

## 5. Conclusion

Bulk deposition was 30–130% higher ( $p < 0.02$ ) than the wet deposition of all major ions, with the exception of  $NH_4^+$ . The acidity of bulk precipitation was significantly ( $p < 0.06$ ) lower than the acidity of wet-only precipitation. Therefore, wet-only samplers are preferred for accurately determining wet deposition fluxes. Alternatively, bulk measurements should be corrected for dry deposition onto the funnels by site-specific bulk over wet-only factors. The chemistry of wet-only precipitation was almost identical at the two study sites with a different height that were located about 1 km from each other. A small but significant difference in wet-only deposition between the sites was only found for  $NH_4^+$  and  $NO_3^-$ , which could be attributed to the delayed closing of the wet-only lid by the electrical, resistance-driven rain sensor at one site. The measured bulk/wet-only ratios show that the major fraction of the studied ions was removed from the atmosphere by wet deposition rather than by dry deposition, except for  $K^+$ . Bulk deposition exceeded the wet acidifying deposition of  $SO_4^{2-}$ ,  $NO_3^-$ , and  $NH_4^+$  by less than 25%. Yet, bulk collectors do not provide reliable estimates of the total wet and dry deposition, as the collection efficiency of bulk samplers for trace gases

and submicron particles is substantially different from that of a natural landscape.

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