

Fog deposition fluxes of water and ions to a mountainous site in Central Europe

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(Manuscript received 13 June 2006; in final form 2 April 2007)

ABSTRACT

Fog and precipitation composition and deposition were measured over a 1-yr period. Ion concentrations were higher in fog than in precipitation by factors of between 6 and 18. The causes of these differences were less dilution of fog water due to non-availability of condensable water vapour, and more efficient transfer of surface emissions to fog water as compared to rain water or snow. Fogwater and dissolved ions depositions were measured with eddy covariance in combination with a bulk fogwater collector. Annual fogwater deposition was 9.4% that of precipitation. The annual deposition of ions through fog was of the same order as that for precipitation. Ammonium, representing local emission sources, had 46% more annual deposition through fog than through precipitation. The fog droplet number and mass size distributions are reported. Fog droplets of 15 μm diameter contribute most to the deposition flux. The variability of processes and parameters contributing to deposition of ions through fog (ion concentrations in fog water, liquid water content in air, fog duration and turbulence) is high.

1. Introduction

The deposition of fog (occult deposition) contributes significantly to the hydrologic, nutrient and pollutant cycles in mountainous regions (see Dollard et al., 1983; Marloth, 1906, for early examples). It has been recognized that high concentrations of solutes in fog water lead to occult deposition of these substances that can be as high, or higher, than the deposition through rain and snow, particularly in mountainous regions (e.g. Igawa et al., 1998; Herckes et al., 2002; Lange et al., 2003). However, the experimental quantification of these fluxes is still a challenge in atmospheric science and ecosystem research. For many years, passive devices were employed, and similarity between the collection efficiencies of these collectors and the natural surfaces was more or less assumed (see Kulshrestha et al., 2005, for a recent example) with unknown uncertainty. Other approaches, for example weighing plants (Trautner and Eiden, 1988; Fowler et al., 1990), proved unfeasible for various, mainly logistic reasons. Modelling the deposition flux of fog water (Lovett, 1984; Pahl 1996) and multiplication of these fluxes with the concentrations of constituents to predict their deposition fluxes (Elias et al., 1995), is associated with large uncertainties (Klemm

et al., 2006). A direct quantification of the turbulent deposition flux of fog droplets was applied by Beswick et al. (1991), Gallagher et al. (1992), Vong and Kowalski (1995), Vermeulen et al. (1997) and Kowalski and Vong (1999). These experiments were of short duration and thus were not suited to study seasonal variation or yearly budgets. We present results of a 1-yr study of direct measurement of fogwater deposition fluxes at a mountainous ecosystem research site in NE Bavaria, Germany. We applied the eddy covariance method in combination with a fog collector. Together with the chemical composition of the fog water, the deposition flux of constituents was determined and compared to the deposition of water and compounds through wet deposition (rain and snow).

The scope of this contribution is to present the main results of concentrations and fluxes of the long-term study. We highlight the enrichment of concentrations of various ions in fog versus precipitation (rain and snow) and evaluate their role in occult deposition. Processes and parameters leading to large deposition fluxes of water and constituents are shown and discussed.

2. Material and methods

2.1. Experimental site

The Waldstein ecosystem research site (Wrzesinsky and Klemm, 2000, Matzner et al., 2004) is a spruce forest in NE Bavaria (southern Germany, 50° 08' 32" N, 11° 52' 04" E, 775 m a.s.l.) within the Fichtelgebirge mountain range. A 30 m walk-up

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DOI: 10.1111/j.1600-0889.2007.00287.x

scaffolding tower within a stand of 19 m canopy height serves as an experimental platform for various meteorological experiments. The high frequency of fog events throughout the year suggests that occult deposition plays an important role in the nutrient and pollutant budgets of that site.

2.2. Employed instruments

An eddy covariance setup was employed to measure turbulent exchange fluxes of fog water. The setup is described by Burkard et al. (2002) and only briefly outlined here: A Young 81000 ultrasonic anemometer was combined with a fast, high-resolution droplet spectrometer FM-100 (Droplet Measurement Technologies, Inc.), covering droplet diameters from 2 to 50 μm . The spectrometer was mounted at 31 m above ground level on a rotating platform and was pointed into the wind to establish isoaxial sampling conditions. The rotation was adjusted every 10 min on the basis of the measured wind direction. The data collection rate was 8.6 Hz, and data were integrated over 30 min intervals for eddy covariance. Data for liquid water content (LWC) were derived from the FM-100 signals.

Sedimentation, that is, gravitational settling of fog droplets, a non-turbulent flux, was calculated from Stokes' law.

An active, automated sampler was employed to collect fog water on an event basis for chemical analysis. It is a modified version of the Caltech active strand cloudwater collector and the heated version developed subsequently (Daube et al., 1987; Demoz et al., 1996). Our collector has a sampling area of 650 cm^2 . Teflon® tubing (1.5 mm outer diameter) was used as strand material, and a 0.6-mm heating wire was inserted into the tubing. The mean air speed within the collector was 8.1 m s^{-1} . The collection efficiency of the collector as function of droplet diameter was calculated after Davidson and Friedlander (1978) and Demoz et al. (1996). The cut size diameter of a droplet collection efficiency of 50% is 7.3 μm . The maximum collection efficiency for large droplets is 88%. The collector was, together with the FM-100 droplet spectrometer (see above), automatically operated whenever the visibility dropped below 500 m. We used this operational definition, deviating from the general definition of fog (visibility < 1000 m according to the standard of the World Meteorological Organization), because at visibilities between 500 and 1000 m, fogwater amounts sufficient for chemical analysis were generally not collectable. We did not operate the fog collector for extended time periods without actually collecting water, in order to minimize cross-contamination. The fog collector worked reliably and unattended even under cold winter conditions. For most of the experimental period, the maximum duration for single fogwater samples was set to 8 h to avoid potential overflow of collection containers. The fog collector was installed at an altitude of 24 m above ground level.

Chemical analyses were performed using standard procedures (Thalmann et al., 2002). For the quantification of fogwater deposition fluxes of ions for a single event, the concentrations of

ions in the respective bulk fog sample was multiplied by the total fogwater flux, as summed over the time period of the event.

A wet-only precipitation (rain and snow) sampler (Umlauf and McLachlan, 1994) was operated at the site. The samples were collected weekly, quantified, and analysed for ions (Matzner, 2004). The fog deposition study was performed from 18 September 2000 to 5 December 2000, and from 17 April 2001 to 18 March 2002. Data from the second period only are analysed in this contribution. For comparison, wet-only precipitation data are available for the period from 2 April 2001 to 25 February 2002. Visibility, an indicator of the presence and density of fog, has been measured at the site since December 1996.

2.3. Uncertainties

Fogwater fluxes, as measured with eddy covariance, need to be interpreted with caution. While the instrumental errors are estimated to be small (Klemm et al., 2005), liquid water vertical flux divergence and convergence have been observed (Kowalski and Vong, 1999; Burkard et al., 2002) and potential causes were discussed. At our site, lower flux densities were observed at the lower level and closer to the canopy (Burkard et al., 2002). As fog is not typically associated with uphill winds, we believe that (partial) evaporation of droplets during turbulent deposition is the cause for the observed divergence (less flux at the lower level). The occult deposition of fog water to the canopy is thus likely to be somewhat lower than estimated by the eddy covariance technique. A more detailed analysis of the energy budget (not performed with our data set) should help to find the causes of these phenomena.

For the ions dissolved in fog water, the phase change of water should not affect the measured vertical fluxes (Thalmann et al., 2002). Partial evaporation of droplets will lead to lower LWC and higher concentrations. The ion deposition flux, which is the product of liquid water flux and the concentration, will not be affected. This holds at least as long as the fog droplets do not migrate into, or out of, the size range at which they are collected for chemical analysis. The critical size range is, in our case, in the order of 8 μm diameter.

However, the vertical separation of the eddy covariance setup (31 m above ground) and the fogwater collector (24 m) may have led to the effect that a higher liquid flux was multiplied with a higher concentration of ions. Measuring both parameters at the same height might have led to smaller products (ion deposition fluxes), so that our results may overestimate the true flux.

3. Results and discussion

3.1. Fog characteristics

Fog has occurred on average 200 d per year since 1997. The lowest frequency occurred in 1999 (164 d), the highest in 2001 (233 d). The site is within fog about 20% of the time; the foggiest month is November (38%), the least foggy month is August (7%).

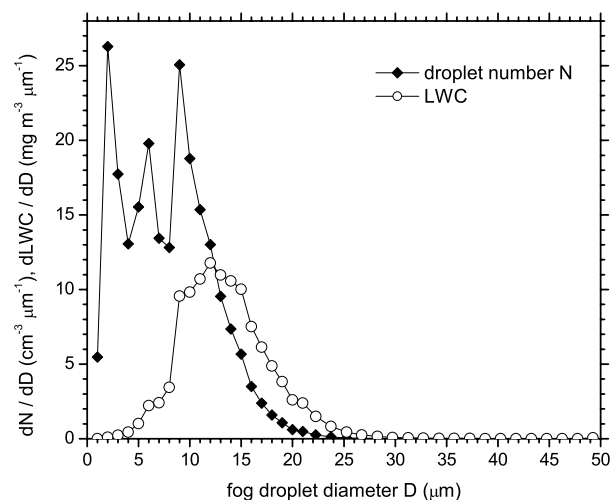


Fig. 1. Distribution of droplet number N (filled diamonds) and fog liquid water content LWC (open circles) in the size spectrum of fog droplets, 17 April 2001 – 18 March 2002. Medians of all 5-min intervals with fog are shown.

As the site is at a relatively high altitude in a mountain range, most fog events are associated with clouds being advected from westerly directions, and hitting ground at the site (intercepted stratus). These fog events are typically associated with relatively high wind speeds and thus with a generally well developed turbulence. In contrast, local or regional radiation fog events are rare.

The fog droplet number size distribution shows that most droplets are of diameters between 2 and 9 μm (Fig. 1). The highest contribution to the LWC , however, originates from droplets of 9 to 15 μm diameters, with still significant contributions of droplets up to about 20 μm diameters. Size distributions exhibit a large variability between events and within single events (not shown).

For fog events with visibilities < 500 m, average LWC 's were computed from the fog spectrometer data. The median LWC was

156 mg m^{-3} , with the 5th and 95th percentiles being 1.4 and 523 mg m^{-3} , respectively.

3.2. Fog and precipitation chemistry

Precipitation and fog chemistry have undergone significant changes in Central Europe over the past decades. Decreasing emissions of air pollutants, mainly oxides of sulphur and nitrogen, has led to a decrease in air pollution (Klemm and Lange, 1999), including the acidity of the atmospheric aqueous phase (Lange et al., 2003). Median fogwater ion concentrations of this study (Table 1) are somewhat lower than those collected in 1997, and much lower than earlier fogwater concentrations from the same area (Wrzesinsky and Klemm, 2000), reflecting the general trend.

During the sample period of approximately 11 months in 2001 and 2002, a total of 259 samples were collected, of which 247 could be analysed for pH and ions (Table 1). The ions H^+ , NH_4^+ , NO_3^- , SO_4^{2-} and Cl^- make up 94% of the total equivalent concentrations in fog, and approximately 87% in the precipitation samples. For most fog samples, the ions NH_4^+ , NO_3^- and SO_4^{2-} are, in that order, the most important ionic constituents.

Differences of ionic and other constituent concentrations between fog and precipitation have been reported from experimental sites virtually around the globe (e.g. Post et al., 1991; Schemenauer et al., 1995; Igawa et al., 1998; Lange et al., 2003; Ali et al., 2004; Beiderwieden et al., 2005). In most cases, the enrichment factors (i.e. the ratio of average or median concentration of a substance in fog to the respective concentration in precipitation water) are between about 2 and 7. Unfortunately, we could not compute the median enrichment ratios for Na^+ , K^+ , Mg^{2+} and Ca^{2+} , due to low concentrations in many samples. Of the remaining ions, Cl^- showed the lowest enrichment factor (6.1), while all other enrichments were much larger (medians up to 18.1; Table 1). We interpret the pattern of the ions chloride, sulphate, nitrate and ammonium with respect of the distance of

Table 1. Statistics of major ionic composition of fog and precipitation water at the Waldstein site. Fog represents 247 samples collected between 17 April 2001 and 18 March 2002, precipitation represents 45 samples collected between 2 April 2001 and 25 February 2002. Concentrations are given in units mg l^{-1} , except for pH. 'bdl' means 'below detection limit'. The median ratios are listed as well. For pH, the ratio was computed from the $10^{-\text{pH}}$ equivalent concentrations. 'n.d.' means not determined

	pH	Na^+	K^+	NH_4^+	Mg^{2+}	Ca^{2+}	NO_3^-	SO_4^{2-}	Cl^-
Fog									
5 percentile	3.30	bdl	bdl	1.9	bdl	bdl	4.7	3.6	0.04
50 percentile (median)	4.26	1.2	0.37	11	0.20	0.59	27	14	2.0
95 percentile	5.44	12	1.8	42	1.5	3.6	140	48	16
Precipitation (wet only)									
5 percentile	5.04	bdl	bdl	0.28	bdl	bdl	1.2	0.65	bdl
50 percentile (median)	5.38	bdl	bdl	0.58	bdl	bdl	2.1	1.2	0.32
95 percentile	5.91	0.53	0.33	2.2	0.08	0.64	6.0	3.0	1.4
Median ratio fog/precipitation	13.2	n.d.	n.d.	18.1	n.d.	n.d.	12.7	11.8	6.1

the emission sources of these ions (or their precursors) from our site (Lövsblad et al., 2004): Chloride has a principal source from sea salt and this source is far away from our site in the centre of the European continent. The enrichment of the Cl^- concentration in fog versus precipitation is by a factor of 6.1. Sulphate still mainly originates from combustion of fossil fuel and the SO_2 emissions associated with it. These emissions are spread over Europe, with strong influences to our site from industrial areas in western Germany, and from the Bohemian basin to the East of our site. The precursors of nitrate, nitrogen oxides, are emitted from any combustion processes, with road traffic contributing about 50% of the NO_x emissions in Germany (Umweltbundesamt, 2006). The closest larger cities (about 30000 inhabitants) are about 30 km away from the experimental site, with a number of villages and rural roads being closer. A major highway passes by at a distance of 8.6 km to the West. Summarizing, the precursor emissions for SO_4^{2-} and NO_3^- are tens to hundreds of km away from the Waldstein site. The enrichment of NO_3^- and SO_4^{2-} in fog versus rain is by a factor of 12.7 and 11.8, respectively. The highest enrichment was found for the ammonium ion. The precursor of ammonium, NH_3 , is emitted from agricultural sources, which are ubiquitous in the rural area of northern Bavaria. Some farms are closer than 5 km to the site, with a potential impact on the air chemistry. For ammonium, the enrichment is by a factor of 18.1.

For the acidity (here computed as $10^{-\text{pH}}$, or the H^+ ion concentration), the enrichment in fog versus precipitation must be understood on the basis of the ion balance between the acidifying agents sulphate and nitrate on the one hand, and ammonium, resulting from the base ammonia, on the other hand. The difference of the equivalent concentrations ($\mu\text{eq. l}^{-1}$) of nitrate plus sulphate in fog minus that in precipitation is higher than the difference of the ammonia concentration. This leaves room for a significant increase of acidity in fog, which leads to a median enrichment of H^+ by a factor of 13.2 (Table 1).

Igawa et al. (1998) and Beiderwieden et al. (2005) found exceptionally large enrichment factors for NO_3^- (around 30) and NH_4^+ (around 50). While the causes are not perfectly clear, these results tend to support our hypothesis that ions, whose precursors are emitted from the ground and possibly not far away from the fogwater collection site, tend to enrich with the highest factors in fog water. Zimmermann and Zimmermann (2002), measuring in the Erzgebirge mountain range to the NE of our site, found high enrichments (factors about 14) for NH_4^+ and SO_4^{2-} , supporting our hypothesis that local sources of ions (or precursors) lead to increased enrichment in fog water.

We conclude that there are two mechanisms leading to higher concentrations of solutes in fog as compared to precipitation. First, the growth and dilution of fog droplets through condensation may be limited due to non-availability of condensable water vapour. This leads to an enrichment of about a factor of 6 in our case (as observed for Cl^-), and factors between 2 and 7 on a more general scale. Further enrichment to factors of about 12–

14 is due to emissions of precursors and subsequent reactions in the atmosphere, in the distance range of tens through hundreds of km from the site. On top of that, local emissions from the surface are more likely to affect fog than a raining cloud, and may lead to further enhancement of the respective substances (in our case NH_4^+) of fogwater concentrations as compared to precipitation (factor of 18 in our case, even higher enrichments in other studies). Further factors, such as the residence time of fog water in the atmosphere or the time period needed to establish equilibrium between the gas and aqueous phases (Elias et al., 1995), seem not to play a role in the establishment of the fog/precipitation enrichments.

3.3. Fogwater fluxes

For the following, we consider a net downward matter flux as deposition, implying that the material is most likely deposited to the plant surface. Any upward flux from the biosphere to the atmosphere is regarded as an emission flux. Whatever the exact sources and sinks or mechanisms are, a downward (deposition) flux is associated with a negative sign, and an emission flux is positive.

The deposition of fog water is driven by at least two major mechanisms, the turbulent exchange of fog droplets, and gravitational settling. Whereas the settling velocity increases with increasing droplet diameter, the LWC decreases for droplets with diameters $> 15 \mu\text{m}$ (Fig. 1). In combination, droplets with diameters between 9 and $25 \mu\text{m}$ contribute significantly to gravitational settling (maximum at $15 \mu\text{m}$, Fig. 2). The contribution of sedimentation to the total fogwater deposition flux is 14%.

For the turbulent flux it is about the same size range of droplets that contributes to the total flux (Fig. 2). Note that droplets with

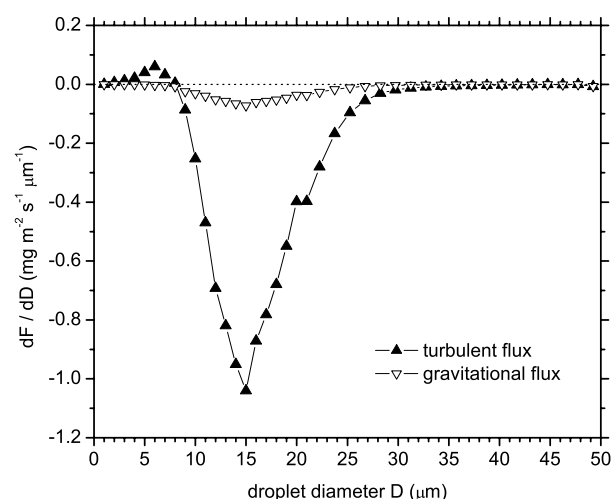


Fig. 2. Turbulent exchange flux (solid triangles) and gravitational settling (sedimentation flux, open triangles) of fog droplets at the Waldstein site. Negative fluxes mean deposition, positive fluxes emission. Average fluxes for all events are shown.

diameters up to $8\ \mu\text{m}$ diameter show a net emission flux. Similar behaviour has been observed by Vong and Kowalski (1995) and Kowalski and Vong (1999), and was mentioned for our site by Thalmann et al. (2002). Migration of droplets within the size spectrum (evaporation or growth by condensation), occurring below the experimental setup (closer to the ground and canopy top than the instruments), must be the cause for this phenomenon. Either large droplets evaporated and thus decreased to diameters of $8\ \mu\text{m}$ or less, or evaporation of water from the relatively warm vegetation and subsequent recondensation on interstitial aerosol led to the formation of new droplets. Further analysis of the occurrence of these fluxes in relation to the cloud itself (top/centre/base of cloud, beginning/middle/end of event) and with respect to the net fluxes of energy and water vapour need to be performed. Observed vertical flux divergence for LWC at our site (Section 2.3) supports the hypothesis that water phase change plays a role during fog deposition. In any event, the magnitude of the emission flux is only 2% of the turbulent deposition of droplets larger than $8\ \mu\text{m}$ diameter. Turbulent deposition is by far the dominating process (Fig. 2).

Fogwater deposition is a significant component of the hydrological budget (Table. 2). For the period of overlapping full-month data from May 2001 to February 2002, fogwater deposition is 9.4% of precipitation. For single months, this ratio varies between 3.6 and 31%.

The variability of the fogwater deposition flux is caused by the variability of physical conditions between events. It is evident that a high LWC should lead to a high deposition flux. This link is confirmed by the Spearman rank correlation coefficient, which indicates a highly significant correlation between these two parameters (left-hand panel in Fig. 3). However, the figure also shows large scatter, clearly indicating that a high LWC is not necessarily associated with a large deposition flux and vice versa.

Like LWC, the visibility is an indicator for the density of fog. The operational advantage of visibility over LWC as an indicator for fog density is the fact that it is easier to measure. The correlation between visibility and LWC has been studied for our sites (Klemm et al., 2005) and was found to exhibit large scatter as well. Its correlation with the deposition (middle panel in Fig. 3) is highly significant, but a large scatter is again apparent. Very large deposition fluxes (more than $1\ \text{l m}^{-2}$ in one event) occurred at visibilities $<200\ \text{m}$. On the other hand, visibilities below $200\ \text{m}$ very often occur together with rather small deposition fluxes.

Fog events lasting over longer time periods should yield more deposition flux. This correlation is shown in the right panel of Fig. 3. As indicated in Section 2.2, the fogwater collector was, for most of the experimental period, programmed to start a new sample after a maximum of 8 h. This leads to an artificial lumping of data points around 8 h fog duration in Fig. 3. The true number of events is smaller than the number of dots shown, and longer fog durations occurred more frequently than shown in Fig. 3.

Although this artefact jeopardizes the correlation between fog duration and fogwater deposition, the correlation coefficient is larger than for LWC or visibility. Longer fog events clearly lead to more deposition.

If the prediction of fogwater deposition from any of the parameters discussed so far would be the goal, a parametrization over the fog duration would apparently lead to the best results.

However, it is also evident that other driving forces than the ones shown play important roles in determining the deposition flux of fog water. Micrometeorological exchange processes, mainly turbulent transport, need to be considered to develop understanding of the deposition process. The correlation between the deposition velocity of fog water and the friction velocity is shown for 30 min average data in Fig. 4. The deposition velocity v_d (m s^{-1}) is the fogwater deposition flux (in this case per time unit, $\text{mg m}^{-2} \text{s}^{-1}$), divided by the LWC (mg m^{-3}). The friction velocity u^* is derived from the ultrasonic anemometer data (e.g. Stull, 1988). A well-developed turbulence regime is expressed through high u^* , along with other variables. As turbulent exchange is the main driver for fogwater deposition at our site (Fig. 2), a high fogwater deposition is expected to be correlated with high u^* . The data confirm a highly significant correlation, however, the scatter is, once again, large (Fig. 4).

Overall, the basic processes and parameters leading to large fogwater deposition fluxes are understood. The contribution of liquid water content (or, indirectly, of visibility), fog duration, and friction velocity, are supported by statistically significant rank correlations between these parameters and the deposition flux of fog water. However, a direct statistical prediction of the fogwater deposition flux from the presented parameters was not considered successful (data not shown), because large scatter still occurs. Complex models need to be employed to predict the deposition of fog water to the forest. More elaborate modelling, using a one-dimensional multilayer approach (Lovett, 1984; Pahl 1996) has been widely applied to various sites. For our site, the deviations of the modelled fluxes from measured fluxes are still very large (Klemm et al., 2005). This leads us to conclude that, despite all difficulties involved, a direct measurement of the fogwater deposition flux with the eddy covariance method leads to the best possible results.

3.4. Ionic deposition

More water is deposited through precipitation than fogwater deposition (Table 2). On the other hand, ion concentrations are considerably higher in fog water than in precipitation water (Table 1). This combination leads to deposition fluxes of ions which are of the same order in fog as in precipitation (Table 2). For NH_4^+ , the total deposition through fog is 46% larger than that of precipitation, and for acidity, fog deposition yields twice the amount of precipitation. For other mountainous sites at similar altitudes, ion deposition through fog was found to be lower than (10–28%, Herckes et al., 2002; up to 50%,

Table 2. Monthly deposition fluxes of water ($\text{kg m}^{-2} = \text{mm}$) and major ions ($10^{-4} \text{ g m}^{-2} = \text{g ha}^{-1}$ for H^+ , $10^{-4} \text{ kg m}^{-2} = \text{kg ha}^{-1}$ for all other ions) at the Waldstein site. 'n.d.' means 'not determined'

Month	H_2O		H^+		NH_4^+		NO_3^-		SO_4^{2-}		Cl^-	
	Precipitation	Fog	Precipitation	Fog	Precipitation	Fog	Precipitation	Fog	Precipitation	Fog	Precipitation	Fog
April 2001 ^a	97	0.3	6.9	0.54	1.5	0.060	4.3	0.16	2.0	0.072	0.17	0.0046
May 2001	23	7.2	0.60	1.6	0.25	0.78	0.67	1.8	0.45	0.96	0.063	0.059
June 2001	110	5.2	3.6	1.8	0.80	0.70	2.2	1.6	1.2	1.0	0.12	0.18
July 2001	130	5.3	5.9	0.94	0.76	0.29	1.7	0.59	1.6	0.46	0.052	0.017
August 2001	28	1.0	1.4	0.080	0.71	0.21	2.1	0.53	0.91	0.24	0.15	0.029
September 2001	170	13	7.8	15	1.1	1.5	3.7	4.3	2.2	2.0	0.51	0.34
October 2001	55	10	2.3	13	0.33	1.1	0.88	3.6	0.64	1.5	0.073	0.27
November 2001	150	21	6.9	19	0.52	1.8	2.4	5.3	1.3	2.4	0.50	0.69
December 2001	210	15	3.4	3.7	0.20	0.35	1.1	0.71	0.61	0.63	0.24	0.089
January 2002	110	24	6.1	21	0.50	0.72	1.7	2.3	1.2	1.5	0.45	0.31
February 2002	250	15	6.2	12	0.63	1.0	2.3	3.5	1.6	1.5	0.55	0.46
March 2002 ^b	97	5.9	10.3	n.d.	0.66	n.d.	3.0	n.d.	1.3	n.d.	0.10	n.d.
Subtotal (May–Feb)	1236	117	44.2	88.4	5.78	8.48	18.6	24.1	11.7	12.1	2.72	2.49
Ratio fog/precipitation	0.094		1.99		1.46		1.29		1.04		0.90	

^a After 2 April for precipitation, after 17 April for fog.

^b Until 18 March.

Fig. 3. Scatter plots between total fogwater deposition per event (y-axes) and LWC, visibility, and fog duration, respectively. Dots represent single fog events. The Spearman rank correlation coefficients, ρ , are given in each panel. The lumping of data points at 8 h duration (right panel) is explained in the text.

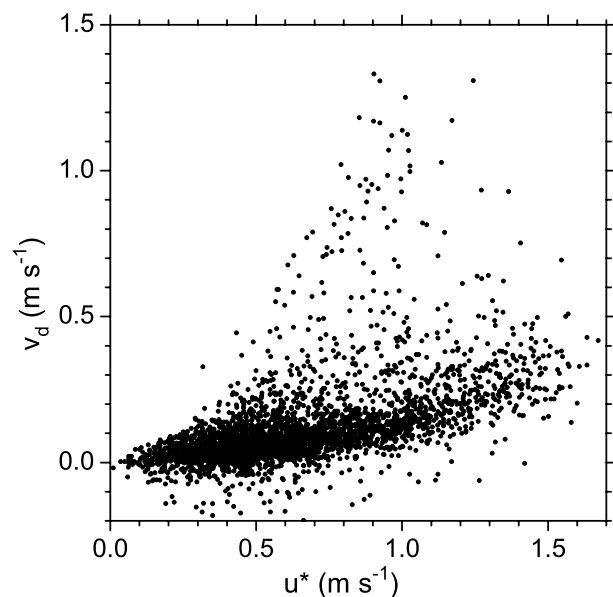
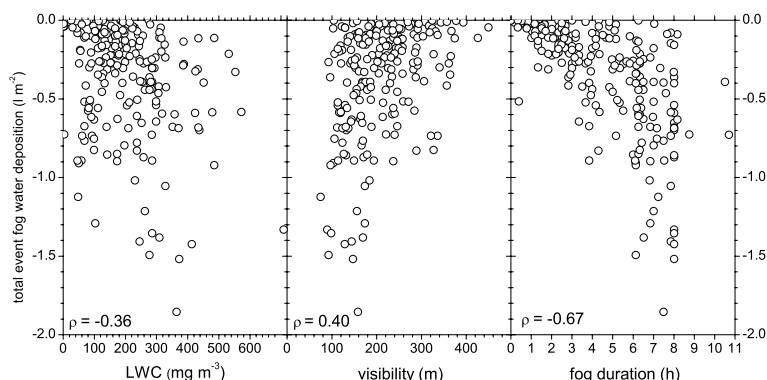


Fig. 4. Scatter plot of the fogwater deposition velocities v_d versus friction velocity u^* . All 30 min averages are shown. A 'negative deposition velocity' corresponds to a net emission flux.

Zimmermann and Zimmermann, 2002) or similar to (Pahl et al., 1994) precipitation deposition. These results were at least in part based on models as discussed in Section 3.3. Our experimental results show that the month-to-month variability of the partitioning of deposition through fog and precipitation are very large. One cause of this variability lies in the variability of the ratio between the deposition of water through fog and precipitation. However, variation of ion concentrations also plays an important role. For example, in December 2001, NH_4^+ deposition through fog was 75% higher than through precipitation, while for nitrate the deposition through precipitation was 55% larger than that through fog.

Due to the high variability of the contributing factors and processes, it is very difficult to generalize these results. For example, fog duration and LWC vary strongly with the altitude above sea level. In the higher mountainous ranges in Central Europe, the potential to contribute higher amounts of fog wa-

ter and constituents increases with altitude (Zimmermann and Zimmermann, 2002). However, rain and snow will also increase with altitude, so that the partitioning between fog and precipitation may vary as well. Rogora et al. (2006) found for sites in the Alps that the contribution of fog to total nitrogen deposition increases with altitude. Whether these results are transferable to the lower mountain ranges in Central Europe is unclear.

The deposition flux of ions is computed through multiplication of the deposition flux of fog water (Section 3.3) with the concentrations of ions during the respective events. Therefore, the variability of the ion deposition fluxes is due to the inter-event variability of either the fogwater deposition fluxes, or the ion concentrations, or both. Figure 5 (left and middle panel) shows the respective scatter plots for NO_3^- .

Between nitrate deposition and concentration (left-hand panel in Fig. 5), the statistical correlation is highly significant ($\rho = -0.32$, $N > 200$, significance better than 99.9%), but the scatter is very large as well. The correlation is stronger between nitrate deposition and fogwater deposition (middle panel). Two other major ions (ammonium and sulphate, details not shown), exhibit almost identical correlations between the deposition fluxes and the concentrations ($\rho = -0.37$ for NH_4^+ , $\rho = -0.32$ for SO_4^{2-}), and between the deposition fluxes and the fogwater deposition flux ($\rho = 0.64$ for NH_4^+ , $\rho = 0.71$ for SO_4^{2-}). The H^+ concentration shows slightly different patterns: For this ion, the correlation between deposition flux and concentration (computed as $10^{-\text{pH}}$) is highest ($\rho = -0.72$), while the magnitude of the rank correlation coefficient between deposition and fogwater deposition is lower ($\rho = 0.56$). We suspect that the larger dynamic range of the H^+ concentration (ratio of 138 of $10^{-\text{pH}}$ between the 95th and the 5th percentile, Table 1, as compared to ratios of 23 for NH_4^+ , 29 for NO_3^- and 13 for SO_4^{2-}), leads to the extraordinarily close correlation between deposition and concentration of acidity.

The best predictor for the nitrate deposition on an event basis is shown in the right panel of Fig. 5: The 'abundance' of nitrate is a combined measure, computed through multiplication of three parameters which can be measured relatively easily: (i) the ion concentration in fog water, (ii) the LWC, as derived from the visibility data from a potential equation valid for our site

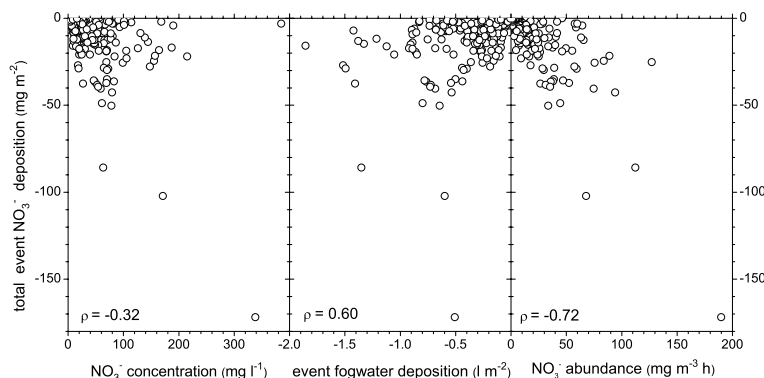


Fig. 5. Scatter plots between nitrate deposition per event (y-axes) and fogwater concentration, fogwater deposition flux per event, and nitrate 'abundance', respectively, for single fog events. Abundance is defined in the text. The Spearman rank correlation coefficients, ρ , are given in each panel.

($LWC = 171.4 \times (\text{visibility}/\text{m})^{-1.45}$, Klemm et al., 2005) and (iii) the fog duration (Fig. 3). This 'abundance' indicates how much nitrate, as dissolved in fog water, was present during an event. The correlation of this abundance with the measured fogwater deposition flux is very good ($\rho = -0.72$). It is in the same range for ammonium ($\rho = -0.69$) and sulphate ($\rho = -0.69$). For acidity, the rank correlation between deposition flux and the abundance is $\rho = -0.84$, the strongest correlation so far.

For the entire experimental phase (Table 2), the relative importance of fog deposition increases in the order chloride, sulphate, nitrate, ammonium, and the acidity. For Cl^- , SO_4^{2-} , NO_3^- and NH_4^+ the same reasoning as for the concentration ratios between fog and precipitation (Section 3.2) leads to the conclusion that the distance of the emission sources of these ions (or their precursors) determines their relative importance in the deposition fluxes: The ion with the closest emission source (NH_4^+) deposits mostly through fog (46% more than through precipitation). For chloride, representing the most distant source, fog deposition is about 90% of the deposition through precipitation. Sulphate and nitrate are in the middle range.

Extrapolating the sum of fog deposition and precipitation fluxes to a 1-yr period, we arrive at estimates of $0.96 \text{ g m}^{-2} \text{ a}^{-1}$ for sulphur (S) from SO_4^{2-} . This is within the range of total S deposition that is estimated from the EMEP model for our region ($0.75\text{--}1.0 \text{ g m}^{-2} \text{ a}^{-1}$, for the year 2003, Klein et al., 2005). This comparison is particularly noticeable since we did not include any dry deposition in our estimate. However, as dry deposition of aerosol particles and gases also plays an important role in the fluxes of oxidized S across the biosphere/atmosphere interface, our results suggest that the EMEP results underestimate the true deposition flux by the (unknown) amount of dry deposition. Further, the canopy balance method that has been applied at our site (Matzner et al., 2004), yields 22% higher fluxes than the deposition of precipitation plus fog for our experimental period, implying that dry deposition is about 22% of wet deposition. We conclude that even that amount is low and that the true total deposition of S is larger than estimated by the canopy balance method.

For nitrogen (N) compounds, the canopy balance method is not reliable because canopy N uptake and chemical and biological

reactions jeopardize the flux estimates. Our flux measurements of N deposition (from NH_4^+ and NO_3^- through precipitation and fog, $4.4 \text{ g N m}^{-2} \text{ a}^{-1}$) is about three times larger than the EMEP estimate ($1.25\text{--}1.75 \text{ g N m}^{-2} \text{ a}^{-1}$ for the year 2003, Klein et al., 2005). The true exchange fluxes of nitrogen compounds remain very uncertain. For further progress in measuring the exchange fluxes of nutrients and pollutants, particularly nitrogen compounds, techniques to study the biosphere/atmosphere exchange flux of aerosol particles and their constituents need to be further developed.

4. Conclusions and outlook

We present a long-term experimental study to quantify the magnitude of fog deposition of water and ions and compare it to water and ion deposition by rain and snow, from spring 2001 through spring 2002. This is the first experimental data set comparing fog and precipitation deposition continuously over a long period (almost 1 yr). The concentrations of ions in fog are much higher than in rain, leading to identical or higher deposition of ions through fog as compare to precipitation. The contribution of fog deposition is generally larger than that estimated in model studies at other sites in mountain ranges of Central Europe. The generalization of these results and their transfer to other sites seems infeasible because the variability of processes and parameters influencing the deposition of fog (LWC, fog droplet size distribution, fog duration, ion concentrations, turbulence) is so large that a parametrization of fog deposition, or modelling, will not achieve high quality results. We conclude that – despite difficulties and limitations as discussed in Section 2.3 – the eddy covariance approach is the best method to quantify fog deposition.

To improve the quantification of fog deposition fluxes, the sample collection technique should be refined and further developed. For many events, we collected one or two fogwater samples, integrating over the entire droplet size spectrum and over up to 8 h of event duration. Intra-event variability of the chemical composition of fog droplets may be high so that a better sample resolution may lead to different results. Both a higher temporal resolution (e.g. on a half-hour basis) and a size-resolved

collection, with at least two size classes of fog droplets (Moore et al., 2004), are suggested.

Studying turbulent fog deposition with the eddy covariance technique is probably not feasible everywhere. Wherever the dominating fog formation process is isobaric cooling on site, as may be typical for bottoms of valleys or flat terrain, the atmospheric stability will jeopardize the application of this technique. Whenever the friction velocity falls below about 0.1 m s^{-1} , the turbulence regime is not well established. At our site, that was the case only for 1.6% of the time during fog. At sites with a larger influence of radiative cooling and higher stability of the boundary layer, gravitational flux will be more important, and may be directly measured rather than, or in addition to, turbulent exchange.

5. Acknowledgments

We thank J. Gerchau for extensive help during the field campaigns, the central laboratory of the BITÖK for chemical analyses, and S. Frolking for language-editing of the manuscript. The studies were supported by the German federal ministry of education and research (BMBF) through grants PT BEO 51_0339476 D and by the German Science Foundation (DFG) through grants Kl 623/4. Three anonymous reviewers helped to improve the manuscript.

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