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# Summertime fog chemistry at a mountainous site in central Europe

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## Abstract

In this paper, 1997 atmospheric visibility data as an indicator for the presence and density of fog at our ecosystem research site in the Fichtelgebirge mountains, Central Europe, are presented. At this location (about 800 m a.s.l.), fog occurred on 50% of the days and added up to a total fog duration of 1158 h in 1997. Using the visibility as a determining parameter, an automatic system for the collection of fog water was developed, including an automatic sampler, and sampling on an event basis. The data from the summer 1997 season exhibit a large variability in the chemical composition of fog. Easterly winds were associated with fog with higher concentrations of the major ions ( $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ) and metals than westerly winds. Although the  $\text{H}^+$  concentrations are lower than concentrations measured between 1983 and 1988 in NE Bavaria, it is not clear from our data alone if the negative trend over time is significant. A simple parameterization of fog deposition shows that fog plays an important role in the water balance of our forests. However, more detailed studies are needed to quantify this input, and the input of pollutants and nutrients to the ecosystems through fog deposition. © 2000 Elsevier Science Ltd. All rights reserved.

*Keywords:* Fog; Fog chemistry; Fog frequency; Air pollution

## 1. Introduction

The physics and chemistry of precipitation have been studied intensively over the last decades. It is well established that acid rain may lead to distortions in ecosystems and to building damage. In Europe, the emissions of the atmospheric precursors of acid rain,  $\text{NO}_x$  and  $\text{SO}_2$ , have been reduced, and the acidity of rainwater has decreased (UBA, 1997). Fog has also been studied for many years (Georgii and Schmitt, 1985; Fuzzi et al., 1992; Winkler et al., 1994; Möller et al., 1996; Choularton et al., 1997), however, studies have often been conducted less frequently and less systematically for two reasons: First, the collection of fog is more difficult and time consuming than the collection of rain; and secondly, fog plays an

important role only in some areas of the world, while it is an unimportant or even negligible phenomenon in other areas (Alt, 1932).

Grunow (1955) and Baumgartner (1958) recognized that in mountain ranges in Central Europe (reaching altitudes in the order of 1000 m a.s.l.), the input of liquid water through deposition of fog droplets may play a significant role in the water balance of forests. Further, it has been documented for our region in Central Europe (Schrimppf et al., 1984; Verhoeven et al., 1987) and various other locations (e.g., Schemenauer et al., 1995) that the concentrations of trace substances (such as acids) in fog are generally higher than they are in rainwater. Therefore, we suggest that fog deposition may also play a significant role in the nutrient and pollutant balance of various mountainous ecosystems. However, most studies in Central Europe are only of episodic nature and in most cases focus on the winter months and, thus, no general picture about fog as a contributor to fluxes of water and trace substances in Central European ecosystems can be drawn so far.

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In this contribution, fog frequency and fog density at our forest research site in Central Europe are analyzed. We present a system that enables us to systematically collect fog on an event basis and we analyze fog chemistry data from the 1997 summer season. Further, we will outline our ideas of how systematic studies should be conducted in the future to study fog chemistry and fog deposition to forest ecosystems.

## 2. Experimental

### 2.1. Site description

Our research site “Waldstein” is situated at 50°08′36.0″N, 11°52′06.6″E at 786 m a.s.l. (ground level) in the Fichtelgebirge mountains in northeastern Bavaria, Germany (see map in Fig. 1). These mountains reach peak altitudes up to 1051 m a.s.l. and represent a rural Central European location. The vegetation cover is dominated by spruce forests (*Picea abies* (L.) Karste), which exhibit intense symptoms of forest decline (cf., Schulze et al., 1989; Matzner et al., 1998).

Most of the time, the air chemistry is governed by the zonal circulation that carries marine air masses over western and Central Europe before arrival at our site. Less frequent are situations with northerly or easterly winds that advect continental air masses. These continental air masses normally carry higher concentrations of primary air pollutants such as SO<sub>2</sub> that were emitted from lignite burning power plants in Northwestern Bohemia (Czech Republic) to the East of our site, and in the Halle-Leipzig industrial area to the North, respectively (Klemm and Lange, 1999). Road traffic in the Fichtelgebirge mountains is, compared to the average in Germany, low.



Fig. 1. Section of Central Europe with the box highlighting our research area (source: PCL map collection on the internet, Univ. of Texas, Austin).

We collected fog samples on a 30 m high meteorological tower at a level of 24 m, i.e., about 5–10 m above the tree canopy. The tower is located at a distance of about 650 m from the next mountain peak (852 m a.s.l.) on a South exposed slope (5° inclination). The visibility was measured about 300 m west of the tower in a 100 m × 200 m forest clearing in a height of 4 m above ground (770 m a.s.l.). This location was chosen for technical reasons (accessibility of telephone line for remote data transfer, etc.).

### 2.2. Data acquisition and fog collection

The visibility as an indicator for the presence and density of fog was measured with a *Vaisala PWD11* Present Weather Detector. This instrument measures the scattering of near-infrared light by aerosol particles (such as fog droplets). The measurement range is between 10 and 2000 m, which is a typical range for visibilities during foggy conditions. The accuracy and precision are  $\pm 20$  and  $\pm 5\%$ , respectively (PWD 11 manual). Fog water was collected with a modified Caltech Active Strand Cloudwater Collector (CASCC: Daube, 1987; Klemm et al., 1992), with the fog water directly flowing into a Teflon PFA 1 l sample bottle. The collector was operated with 230 VAC at a flow rate of 1150 m<sup>3</sup> h<sup>-1</sup>. Fog water sampling rates were between 0.11 and 7.2 ml min<sup>-1</sup> (mean: 1.5 ml min<sup>-1</sup>).

The fog collector was remotely switched on and off using the output of the visibility gauge: Whenever the visibility was below 500 m, the CASCC was activated, and it was switched off when the visibility reached values above 500 m. Any switching was accompanied by an E-mail that was automatically sent to the scientists at the University of Bayreuth to ensure that fog samples could be collected within short time periods after completion of sampling. 60% of all samples were taken within 3 h after the end of the respective event (maximum was 52 h). After the retrieval of the fog water the collector was cleaned using double-demineralized water. In order to keep the CASCC clean during longer non-fog periods, it was additionally washed once per week as described before. During longer fog episodes, daily samples were taken while in all other cases each sample represents one event. As the CASCC was not heatable, sample collection was limited to conditions with air temperatures above freezing. Therefore, fog was collected between 24 April and 26 October 1997.

Sample volumes up to 250 ml were transferred into and stored in precleaned (ultrapure 0.1% HNO<sub>3</sub> and double-demineralized water) PFA bottles. Surplus sample volumes (up to 1 l total per sampling event) were stored in precleaned (double-demineralized water) HDPE bottles. The samples were stored at  $-18^{\circ}\text{C}$  until chemical analyses.

### 2.3. Chemical analyses

Measured chemical parameters were pH, specific electrical conductivity  $\chi_{20}$ , the concentrations of major ions ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ), and metals (Al, As, B, Cd, Cu, Hg, Mo, Ni, Pb, Sb, Sn).

pH was measured using an potentiometric electrode (Mettler Toledo Inlab 406) with automatic temperature correction. Specific electrical conductivity was determined by an electrode (Metrohm Conductometer E587) and scaled to 20°C. Repeated measurements of samples showed a precision within  $\pm 0.02$  units for pH, and within  $\pm 3\%$  for the conductivity, respectively. Both pH and electrical conductivity were measured in an aliquot of the original sample.

A coupled ICP-AES (inductively coupled plasma – atomic emission spectroscopy) system was used to measure cations (except  $\text{NH}_4^+$ ), and ion chromatography for all other ions. Samples were analyzed after filtration (0.45  $\mu\text{m}$  cellulose acetate). Used methods have standard errors of 1.2–3.9% (depending on the ion). Determination limits for all analyzed ions are listed in Table 1.

Metal concentrations were determined using atomic absorption spectrophotometry (AA). Aliquots of the sample (30 ml) were acidified with 2 ml  $\text{HNO}_3$  (ultra-pure) and irradiated with UV.  $\text{H}_2\text{O}_2$  was added until no further gas production was observed. This extraction lasted up to 48 h. Then the aliquot was used for analysis.

For three blank samples, double-demineralized water was sprayed into the running fog collector. The first blank sample was taken after a regular fog sample was retrieved (dry collector), next one was taken after a period of one week without fog, and the last one after the cleaning of the collector. In blank 3 (after cleaning) no ion had a concentration above detection limit, while blank 2 showed contaminations for some of the ions (Table 1).

Table 1  
Determination limits of ICP-AES and IC, and the maximum ion concentrations for blank sample No. 2 (maximum blank concentration)

Ion	Determination limit $\mu\text{eq l}^{-1}$	Blank 2 $\mu\text{eq l}^{-1}$
$\text{Na}^+$	8.7	< 8.7
$\text{K}^+$	6.7	9.9
$\text{Mg}^{2+}$	2.3	9.8
$\text{Ca}^{2+}$	5.7	48.8
$\text{NH}_4^+$	21.1	29.8
$\text{Cl}^-$	13.3	< 13.3
$\text{NO}_3^-$	7.3	50.7
$\text{SO}_4^{2-}$	6.0	52.1
$\text{PO}_4^{3-}$	2.7	< 2.7

Blank 1 was only contaminated by  $\text{Ca}^{2+}$  (20.8  $\mu\text{eq l}^{-1}$ ) and  $\text{SO}_4^{2-}$  (24.4  $\mu\text{eq l}^{-1}$ ). It can be concluded that there were no measurable blank concentrations of the ions that resulted from the collector or sample handling. Only atmospheric deposition of particles to the strings of the fog collector during extended dry periods may lead to significant blank concentrations. We tried to avoid such contaminations to the largest possible degree by frequent cleaning of the fog collector.

## 3. Results and discussion

### 3.1. Fog frequency

The frequency of fog events is much higher at the higher altitudes of the mountain ranges in Central Europe than at lower altitudes (Alt, 1932). Most of the fog events are formed by clouds that are advected to the mountain ranges. In Fig. 2, the number of days with fog (at least 10 min of fog) and the total fog duration per month during the year 1997 are presented. Fog events are more frequent and longer during the winter months (mid-October through March) than during the summer months. The seasonal variation of the fog frequency reflects the general meteorological conditions, with low temperatures and high air humidities favoring the formation of fog during winter. Air humidity was  $90 \pm 10\%$  (15 d-average) in January–March and October–December, and  $75 \pm 8\%$  from April to September, respectively.

In total, 183 days with the occurrence of fog during 1997 were observed. For the lower locations such as the city of Bayreuth (350 m a.s.l.), about 40 foggy days per year are typical as a long-term average (Alt, 1932; Trautner, 1988). This difference is due to the occurrence of advective clouds at the mountain site. Note, that the year was relatively dry (538 mm precipitation in 1997 at the Waldstein research site) compared to the preceding years (average 1994–1996: 1105 mm). In Table 2, the duration of fog for various visibility classes is presented. In total, fog added up about 15% of the time during 1997, and of these foggy time periods, dense fog (visibility < 200 m) accounts for about 40%.

In Fig. 3, an analysis of the frequency of the wind directions at our research site during 1997 (left panel), and the frequency during fog (right panel) is presented. The used anemometer is situated on the top of the meteorological tower (32 m above ground). Low wind conditions ( $< 1 \text{ m s}^{-1}$ ) were excluded from this analysis. It becomes evident that fog occurred with an enhanced relative frequency during westerly winds. The zonal circulation frequently advected clouds that met the mountain ranges and led to fog at these locations. Easterly winds very often advected relatively dry continental air masses and fog is a relatively rare event under these conditions.

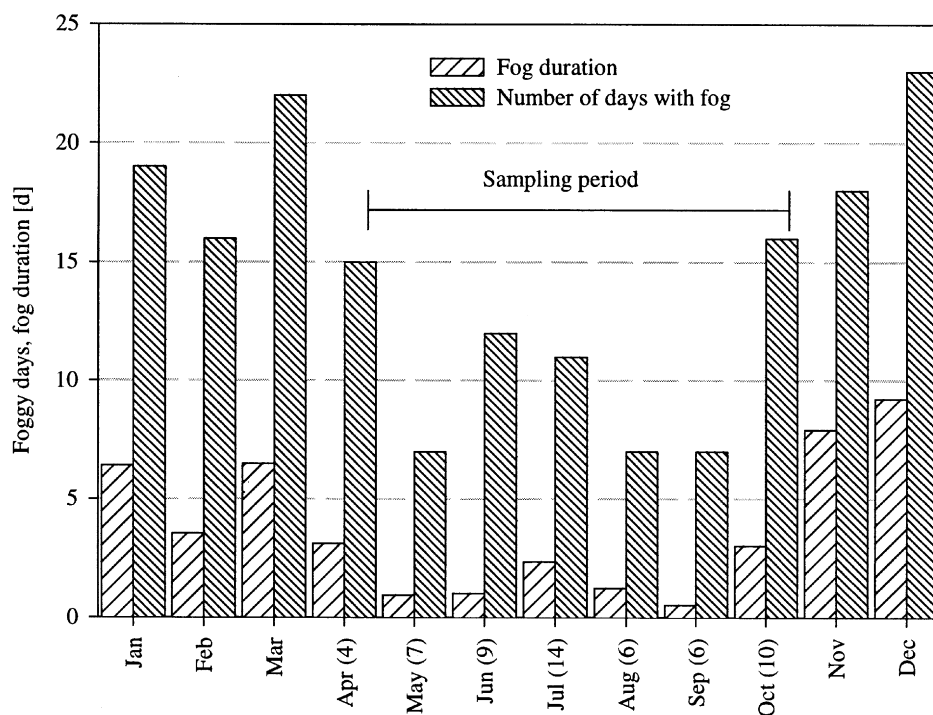


Fig. 2. Number of foggy days and monthly fog durations in 1997 (visibility  $\leq 1000$  m); the number of fog samples taken in the respective month are shown in brackets.

Table 2  
Total duration of foggy conditions (in 4 density classes) in 1997

Visibility	Duration	Percentage for total record 1997 (%)
$\leq 100$ m	93:10 h	1.2
100–200 m	369:40 h	4.8
200–500 m	406:40 h	5.2
500–1000 m	288:00 h	3.7
Total duration	1157:30 h	14.9
Foggy days	183	51.6

### 3.2. Fog chemistry

Within the sampling period, 56 fog samples of 2–1000 ml (mean 315 ml) volume were retrieved. Both the absolute concentration levels and the relative contributions of the various ions to the ion load are highly variable. The total equivalent concentration ranges from 149 to 6760  $\mu\text{eq l}^{-1}$  (median: 1870  $\mu\text{eq l}^{-1}$ ). A statistical characterization of all ion analyses is shown in Table 3. The mean relative composition of the fog samples is shown in Fig. 4. Ammonium ( $\text{NH}_4^+$ ), nitrate ( $\text{NO}_3^-$ ), and sulfate ( $\text{SO}_4^{2-}$ ) are the dominating ions. Together, they make up approximately 85% of the total ion charge. The precu-

sors of these ions in the atmosphere are predominately emitted from animal farming (86% of  $\text{NH}_3$  emissions in Germany; UBA, 1997), combustion of gasoline and other fossil fuel in road traffic, power plants, and industry (92% of the  $\text{NO}_x$  emissions), and the combustion of sulfur-containing fuel such as lignite in power plants and industrial plants (82% of  $\text{SO}_2$  emissions). The contribution of hydrogen ions to the ion charge is low (median: 3.5%), although in some samples, the contribution was up to 13%. Within the last 15 yr, the pH's of rainwater increased significantly in Germany (UBA, 1997). Since the same processes produce acidity in rainwater and in fog water, a similar trend should be existing for fog in NE Bavaria. However, there are no investigations in Central Europe that could prove the existence or absence of such changes in fogwater chemistry over the years. If we compare our data from 1997 with those obtained in the early to middle 1980s (Table 4), we find higher pH's for means, maxima, and minima. However, the sampling sites were at various altitudes a.s.l. and therefore not necessarily directly comparable. It is not clear from this analysis to what degree the possible reduction of the acidity is (i) due to the fact that the earlier measurements were taken in winter and the ones in 1997 during summer; (ii) due to a possible trend of fog acidity over the years; or (iii) due to annual variations that cannot be quantified with a one

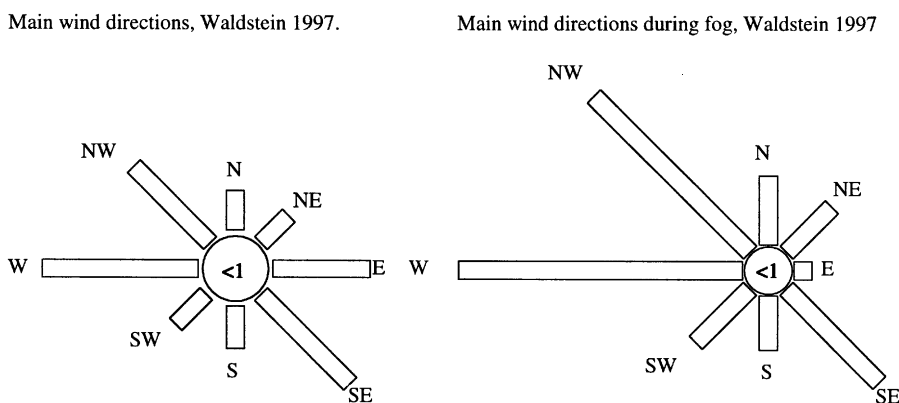


Fig. 3. Frequency of all main wind directions in 1997 (left panel) and frequency of main wind directions associated with foggy conditions (right panel). The inner circles represent the frequencies of conditions with low wind speeds ( $< 1 \text{ m s}^{-1}$ ). The area of the bars and circles is proportional to the relative wind frequencies.

Table 3

Statistical characterization of the chemical composition of our fog samples, and data for “easterly” (N through SE) and “westerly” (SW through NW) wind directions ( $<$  means below the given determination limit;  $\bar{x}$  is the arithmetic mean;  $x_{\text{med}}$  is the median;  $x_{\text{log}}$  is the mean derived from the logarithm,  $x_{\text{min}}$  is the minimum,  $x_{\text{max}}$  is the maximum,  $\sigma$  is the standard deviation, confidence level for Student’s  $t$ -test for different means)

	$x_{20}$ $\mu\text{S cm}^{-1}$	pH	$\text{H}^+$	$\text{Na}^+$	$\text{K}^+$	$\text{NH}_4^+$	$\text{Mg}^{2+}$ $\mu\text{eq l}^{-1}$	$\text{Ca}^{2+}$	$\text{Cl}^-$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$	
Waldstein	$\bar{x}$	151	4.3	89	65	11.5	669	19.5	69	54	481	497
	$x_{\text{med}}$	142	4.3	52	30	9.7	547	10.0	40	31	409	421
	$x_{\text{log}}$	121	4.3	51	39	13.8	547	14.8	46	46	342	376
	$x_{\text{min}}$	17	3.3	2	$< 9$	$< 6.7$	$< 21$	$< 4.6$	$< 11$	$< 13$	20	55
	$x_{\text{max}}$	452	5.7	513	664	68.5	2580	152	493	389	1740	1800
	$\sigma$	95	0.5	91	124	10.5	498	29.6	84	74	370	360
“Easterly”	$x_{\text{log}}$	189	4.0 <sup>c</sup>	101	<sup>a</sup>	<sup>a</sup>	788	14.0	74	<sup>a</sup>	596	690 <sup>c</sup>
“Westerly”	$x_{\text{log}}$	100	4.4 <sup>c</sup>	41	<sup>a</sup>	<sup>a</sup>	463	15.7	40	<sup>a</sup>	268	395 <sup>c</sup>
Confidence level		$> 99\%$		$> 99\%$	<sup>a</sup>	<sup>a</sup>	$> 99\%$	<sup>b</sup>	$> 99.9\%$	<sup>a</sup>	$> 99\%$	$> 99\%$

<sup>a</sup>Data are not normally or lognormally distributed. No calculations were performed.

<sup>b</sup>No significant difference.

<sup>c</sup>Arithmetic mean.

season data set. The emissions of  $\text{SO}_2$  in Central Europe decreased by about 60% between 1980 and 1994 (UBA, 1997; EMEP, 1997), and a resulting decrease of the air concentrations is observable in NE Bavaria (Klemm and Lange, 1999). However, we found no significant difference in the sulfate content of the fog water, at least if we compare our data with those from the “Ochsenkopf” site which is located at 1024 m a.s.l. and 13 km to the South of our Waldstein site.

Fig. 5 presents an analysis of some of the mean ion concentrations in our fog samples as a function of the respective wind direction. In Table 3, characteristic concentrations for “westerly” and “easterly” winds and the confidence level for the difference (Student’s  $t$ -test for different means) are presented. The numbers of analyzed

samples for “westerly” and “easterly” winds are 38 and 14, respectively. It can be seen that for the ion sum (represented by the electric conductivity) and for the single ions  $\text{H}^+$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$ , respectively, that the concentrations were much higher during easterly winds than during westerly winds. For  $\text{SO}_4^{2-}$ , this phenomenon can easily be explained by the fact that in the Czech Republic, which is to the East of our research site, the  $\text{SO}_2$  emissions from lignite-burning power plants are still high, while the  $\text{SO}_2$  emissions in western Europe have been drastically reduced since the mid 1980s. However, emission patterns offer no obvious explanation for higher  $\text{NO}_3^-$  and  $\text{NH}_4^+$  concentrations during easterly winds. Although reliable emission data are poorly available for eastern Europe, we suggest that the emissions of

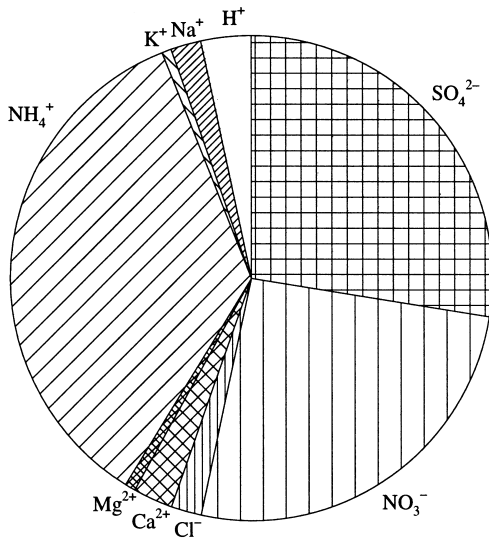


Fig. 4. Median relative equivalent composition of our fog samples.

$\text{NH}_3$  and  $\text{NO}_x$  are not enhanced as much compared to the West as for  $\text{SO}_2$ . It is probably the generally different meteorology that favors higher concentrations during easterly winds: At our site, easterly winds advect air masses that have traveled over large parts of the Eurasian continent and carry less humidity. Therefore, the fog frequency during easterly winds is low (see Fig. 3). We hypothesize that when these winds are associated with fog, the fog is less dense (lower liquid water content) and exhibits relatively small droplets. Therefore, the concentrations of solutes originating from surface emissions are high. On the other hand, westerly winds often carry large amounts of humidity from the North Atlantic Ocean and the North Sea, leading to heavy and frequent rainfall and to a higher fog frequency and liquid water content at our site. We suggest that in these air masses, the fog droplets tend to be larger and therefore exhibit generally smaller concentrations of solutes than easterly winds.

Exceptions from this rule are the  $\text{Na}^+$  and  $\text{Cl}^-$  concentrations which are much higher for some westerly events than for easterly events. The sea salt, originating from the North Atlantic and North Sea, shows a different pattern than the ions reflecting surface emissions ( $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ). For example we found peak concentrations of 558 and 664  $\mu\text{eq l}^{-1}$  of  $\text{Na}^+$  during events No. 44 and No. 48, respectively, which were associated with marine storm conditions. These concentrations represent 16 and 27% of the total ion sum (the median percentage of  $\text{Na}^+$  is only 1.7%).

Aluminum and boron are the dominating metal species in our fog samples (Table 5), copper, lead and nickel are the heavy metals with the highest concentrations.

Table 4  
Comparison of this study with other data from earlier measurements in Northern Bavaria (n.d. means not determined, explanation of statistic terms see Table 3)

	$\bar{x}$	$x_{\text{min}}$	$x_{\text{max}}$	$\bar{x}$	$x_{\text{min}}$	$x_{\text{max}}$	$\bar{x}$	$x_{\text{min}}$	$x_{\text{max}}$	pH	$\text{H}^+$	$\text{Na}^+$	$\text{K}^+$	$\text{NH}_4^+$	$\text{Mg}^{2+}$ $\mu\text{eq l}^{-1}$	$\text{Ca}^{2+}$	$\text{Cl}^-$	$\text{NO}_3^-$	$\text{SO}_4^{2-}$
Waldstein (This study)	151	3.3	2	89	65	11.5	669	19.5	69	54	481	497							
	17	5.7	513	2	<9	<6.7	<21	<4.6	<11	<13	20	55							
	452	3.1	n.d.	513	664	68.5	2580	152	493	389	1740	1800							
Wülfersreuth <sup>a</sup> (Trautner, 1988)	526	2.4	n.d.	n.d.	92	80.2	1370	73.9	375	138	708	1440							
	58	4.9	n.d.	n.d.	12	9.0	87	15.7	51	43	127	352							
	2500	3.5	314	n.d.	774	246	5420	584	3350	660	5600	9040							
Ochsenkopf <sup>b</sup> (Herterich, 1987)	255	2.9	45	314	66	28	922	22	110	96	599	669							
	49	4.3	1190	45	5	4	125	3	9	8	83	83							
	900	3.7	224	n.d.	213	80	2820	76	376	374	2610	2380							
Ochsenkopf <sup>b</sup> (Verhoeven et al., 1987)	175	2.5	n.d.	n.d.	86	37	395	57	151	76	376	415							
Landeshügel <sup>c</sup> (Schrimpf et al., 1984)	69	4.2	n.d.	n.d.	60	n.d.	n.d.	n.d.	50	60	80	310							
	1230				970	n.d.	n.d.	n.d.	2530	1510	3000	2890							

<sup>a</sup>50°03'54"N, 11°45'54"E, 650–680 m a.s.l.

<sup>b</sup>50°01'07"N, 11°48'23"E, 1024 m a.s.l.

<sup>c</sup>50°22.5'N, 11°38.5'E, 600–640 m a.s.l.

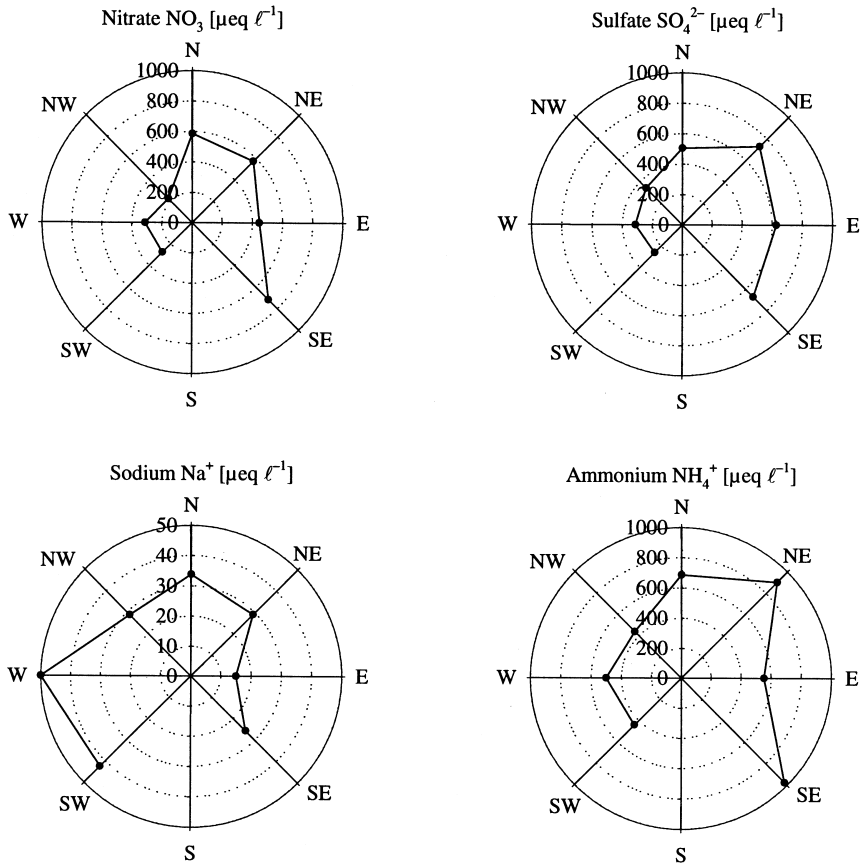


Fig. 5. Ionic equivalent concentrations of our fog events as a function of main wind directions.

Table 5

Characteristic means (as defined in Table 3), minimum, maximum, medians, determination limits, thresholds for drinking water (according to the German Drinking Water Act “Trinkwasserverordnung”), and standard deviations  $\sigma$  for easterly and westerly wind directions of metal concentrations in our fog samples. For Hg, the concentrations were only in three samples above the determination limit. Bold numbers indicate the type of mean used for the  $t$ -test for different means. Confidence levels for the  $t$ -test for different means are only shown when larger than 95%

	Al	As	Ni	Hg	Pb	B	Cd	Cr	Cu	Mo	Sb	Se	Sn
	$\mu\text{g l}^{-1}$												
$x_{\min}$	14	<	0.8	<	3.4	1.7	0.3	<	2.5	<	0.8	1.1	<
$x_{\max}$	903	13.2	42.8	0.4	61.4	80.8	8.7	3.6	56.8	2.0	5.7	11.5	6.9
$\bar{x}$	164	3.1	<b>5.5</b>	0.1	<b>27.6</b>	<b>19.5</b>	1.4	1.1	12.3	<b>0.6</b>	1.9	<b>4.7</b>	2.0
$x_{\log}$	<b>88</b>	<b>2.4</b>	3.8	0.1	20.7	13.9	<b>1.0</b>	<b>0.8</b>	<b>9.7</b>	0.6	<b>1.7</b>	3.8	<b>1.7</b>
$x_{\text{med}}$	88	2.2	4.0		21.5	14.3	1.1	0.8	10.0	0.6	1.5	4.3	1.4
$\sigma$	218	2.9	6.9		17.9	15.8	1.5	0.9	10.0	0.4	1.1	3.0	1.5
Determination limit	3	0.5	1.0	0.1	0.3	1.0	0.1	0.3	1.0	0.2	0.3		1
threshold	200	50	50	1.0	40	5500 <sup>a</sup>	5	50	3000 <sup>b</sup>	N/A	10	10	N/A
N through SE	178	3.2	9.1		40.2	25.8	1.5	1.2	15.1	0.7	1.7	7.4	1.9
NW through SW	62.5	2.0	4.1		19.6	14.7	0.9	0.7	7.9	0.6	1.7	4.2	1.6
Confidence level	>99%		>95%		>99%	>95%	>95%		>99%				

<sup>a</sup>B as  $\text{BO}_3^-$ .

<sup>b</sup>Recommended value.

German drinking water thresholds showing a possible human toxicological impact were exceeded for Pb in 12 out of 37 samples, and for Al in 7 samples (Table 5).

Table 5 further shows an analysis of the metal concentrations as function of the two main wind regimes (winds from N to SE versus winds from SW to NW) during sampling. Because of the limited number of analyzed samples, a more detailed analysis as shown in Fig. 5 for the ions was not possible. For the various metals, we used either the arithmetic mean  $\bar{x}$  or the mean of the log-transformed data ( $x_{\log}$ , as indicated in Table 5) and applied the Student *t*-test for detecting significant differences as shown before for the ions. Most metals show significantly higher concentrations in fog when the winds were from N to SE than from SW to NW. For Pb, we suggest that the still high consumption of leaded gasoline in eastern European road traffic is the reason for enhanced concentrations in fog during easterly winds. For B, it is probably the burning of lignite in power plants in eastern Germany and the Czech Republic that leads to enhanced concentrations during the respective meteorological conditions. Another reason for higher concentrations during “easterly” winds is the enrichment in smaller droplets as described for the ions before.

### 3.3. Fog deposition

The atmospheric deposition of fog (“occult deposition”) plays, in some areas of the world, a significant role in the water, nutrient, and pollutant budgets of ecosystems (e.g., Bruijnzeel and Procter, 1995), including some of the mountain ranges in Central Europe (Grunow, 1955; Baumgartner, 1958; Trautner et al., 1992; Pahl, 1996). The relative role of fog deposition as compared to wet deposition (from rain) is probably higher for trace substances (such as ions) than for water, because the concentrations are normally higher in fog water than in comparable rainwater (Schrimppf et al., 1984; Schemenauer et al., 1995). However, a precise quantification of occult deposition is difficult. Pahl (1996) estimates a contribution between 8 and 52% of occult deposition to total deposition (wet, occult, and dry) at sites comparable to our site in Central Europe. Trautner (1988) measured the deposition of fog to a spruce tree by weighing a sapling continuously through the duration of a fog event in a nearby spruce forest (Wülfersreuth, see Table 2). For technical reasons, this type of experiment was limited to small trees. Trautner (1988) found specific deposition rates DR of 0.16–0.39 g H<sub>2</sub>O m<sup>-2</sup> (leaf area) min<sup>-1</sup> for spruce (*Picea abies* (L.) Karste). If we use these specific deposition rates, a leaf area index (LAI) of between 5.7 and 8.1 for our spruce stand (Alsheimer, 1996), a total leaf area/LAI ratio of 2.57 (Schulze et al., 1989), we can estimate the occult deposition of water to our ecosystem. The respective data are listed in Table 6, where the

water deposited on exposed foliage has been spread over the surface area of the ground to produce an equivalent depth of water. According to this first guess, the contribution of fog deposition to total deposition is in the order of 20–50% for water. Although this analysis is associated with large uncertainties, we believe that the fog deposition of water is significant at our sampling site and can contribute 20% or even more to the atmospheric input of water in 1997. A more detailed estimation of fog deposition should include direct measurements (Vong and Kowalski, 1995; Kowalski et al., 1997; Vermeulen et al., 1997), and modeling of terrain effects, meteorological parameters (wind, LWC), and more specific plant data (Walmsley et al., 1996).

## 4. Conclusions

We have presented physical and chemical data for fog events at our mountain forest research site in NE Bavaria. Atmospheric visibility was incorporated as an indicator for the presence and density of fog into a routine meteorological and air chemistry program. The data from this additional parameter let us conclude that fog is frequent and plays an important, yet underestimated, role in atmosphere/biosphere interaction. We estimated the role of fog in the water balance and found that (i) the uncertainties involved are large because the parameterization is still quite simple, and (ii) that the role of fog is probably very significant, with a possible contribution of fog deposition to total deposition of water of 20% or even more. Because the concentrations of solutes are generally larger in fog than in comparable rain water, fog may play an even more important role in the deposition of these constituents. However, this contribution is more difficult to estimate. Inter-event variability of the chemical composition of fog is very large. We also believe that the fog droplet size distribution, and, as a consequence, the deposition velocity varies quite significantly from event to event. Therefore, it seems not feasible to compute the occult deposition of ions (such as NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, or SO<sub>4</sub><sup>2-</sup>) by simply multiplying the average deposition rate of water (Table 6) with the averages of the ion concentrations (Table 3). We suggest that such estimates should be based on single-event estimates of the water deposition rates and the respective chemical analyses. Vong and Kowalski (1995), Kowalski et al. (1997), and Vermeulen et al. (1997) showed that an eddy-covariance technique is applicable for studying deposition of fog. We suggest that such experiments employing a fast instrument to determine the fog droplet size distribution, should be conducted on a systematic basis, i.e. throughout the entire year. If these studies are supported through measurements of the chemical composition of the fog water, possibly also as a function of the size distribution, we would arrive at significantly improved estimates of the deposition of



Table 6  
Estimation of fog water deposition

	Minimum	Maximum
Leaf area index LAI	5.7	8.1
Deposition rate [DR] of water for <i>Picea abies</i> per leaf area	0.16 g m <sup>-2</sup> min <sup>-1</sup>	0.39 g m <sup>-2</sup> min <sup>-1</sup>
Total fog water deposition of water in 1997 per ground area (1158 h foggy conditions)	163 mm	564 mm
Rain + fog deposition of water in 1997 per ground area	701 mm	1102 mm

water, nutrients, and pollutants to the forest ecosystems through fog.

For fog events associated with easterly winds, emissions in eastern Europe still have a strong influence on the chemical composition of fog water. Although our database is not sufficient for a detailed trend analysis, there are indications that the concentrations of ions in fog have decreased within the last 15 yr.

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