



ATMOSPHERIC RESEARCH PROGRAM FOR STUDYING CHANGING EMISSION PATTERNS AFTER GERMAN UNIFICATION

K. ACKER,*[†] D. MÖLLER,* W. MARQUARDT,[‡] E. BRÜGGEMANN,[‡]
W. WIEPRECHT,* R. AUDEL* and D. KALAB*

*Brandenburg Technical University (BTU) Cottbus, Working Group Air Chemistry, Rudower Chaussee 5, D-12484 Berlin, Germany; and [‡]Institute for Tropospheric Research (IFT), Permoserstraße 15, D-04303 Leipzig, Germany

(First received 24 October 1996 and in final form 17 December 1997. Published July 1998)

Abstract—A dramatic decrease in emission of sulphur dioxide (SO₂, 60%), dust (82%), nitrogen oxide (NO, 30%) and other pollutants (hydrochloric acid (HCl); ammonia (NH₃)) has been observed in East Germany after German unification in 1989. The smaller decrease in total NO is due to significant increase of NO from traffic. Air-pollutant concentrations in both parts of Germany before and after 1989 will be compared and their development will be discussed, based on precipitation and cloud chemistry data from long-term continuous record. Sectoral rain data, based on backward trajectory calculations, clearly show that the significant decline in annual volume weighted precipitation ions (sulphate, calcium, ammonium, chloride) in rain water from sector “East” since 1989 and particularly since about 1992 is roughly correlated with a similar percentage decline in SO₂, dust and NH₃ emissions for the region East Germany.

The acidity of the precipitation from sector “East” has increased very strikingly from 1993 up to 1995 threefold more than from sector “West”. Despite the strong decrease in SO₂ emission, this decrease of the atmospheric neutralising capacity was caused by the much steeper decline in atmospheric base cations in that region. Precipitation data from all transport directions show high variation, but no significant trend in the annual average H⁺ ion concentration. At Mt. Brocken the annual average volume weighted cloud-water acidity during frost-free periods increased by a factor of three between 1992 and 1995. This result, confirmed also by the annual frequency distributions of the pH values, reflects the atmospheric pollutant loading also from all entry sectors. After 1995 this trend is reversed. Detailed classification of the cloud-water data by entry sector, and by meteorological and especially microphysical factors is currently being carried out and preliminary results are presented. © 1998 Elsevier Science Ltd. All rights reserved

Key word index: Emission, trend, precipitation chemistry, cloud chemistry.

INTRODUCTION

Atmospheric acidity is controlled by the balance between acidic and alkaline emissions (Brimblecombe, 1992). Most of these emissions are from power plants based on coal combustion. Emissions of NH₃ neutralise a significant fraction of the atmospheric acids produced from SO₂ and NO_x (Huntzicker *et al.*, 1980). However, alkaline calcium compounds from fly-ash of coal-fired power stations are often the most important neutralising species (Marquardt *et al.*, 1996). For example, Munger and Eisenreich (1983) found 13–35% acid neutralisation by NH₄⁺ and 35 to 79% by Ca²⁺ + Mg²⁺ + K⁺ + Na⁺.

From the end of 1990 until 1995, the wide-ranging integrated project “Scientific Accompanying Program for Recovery of the Atmosphere over the New German Länder (SANA)”, has studied the effects of

restructuring and environmental policy measures in the area of the New German States (the former German Democratic Republic, in the following called East Germany) after German unification. The aim of the first joint environmental program among research groups from East and West Germany (the former Federal Republic of Germany or Old German States) was to track the effect of restoring the atmosphere over East Germany on the chemical composition of the atmospheric multiphase system and the resulting impact on affected ecosystems. Numerical models simulating transport, chemical transformation and deposition of pollutants have been improved and have also been verified with data collected within the project. In this contribution we describe the evolution of the air quality in East Germany using emission data, precipitation (station Seehausen) and cloud-water chemistry (station Brocken) data. Because of their location near the former borderline between East and West Germany (Fig. 1), two regions with different emission patterns (Table 1), these stations are

[†]Author to whom correspondence should be addressed.

excellently suited as measurement points to study the changing air-pollution situation in Germany.

Rates of chemical reactions in cloud water are often faster than in the gas phase and influence the budget

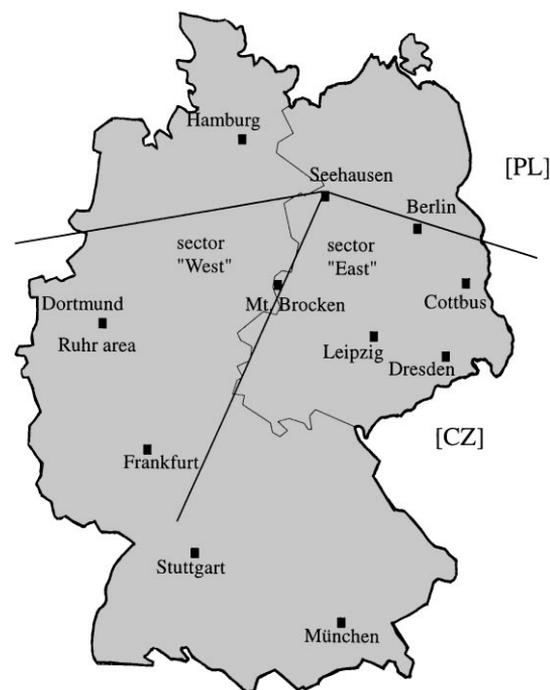


Fig. 1. Locations of the precipitation monitoring station Seehausen and of the cloud water monitoring station Mt. Brocken in Germany.

of acid components, photooxidants and aerosols within the troposphere (Möller, 1980; ten Brink *et al.*, 1987; Chandler *et al.*, 1989; Walcek *et al.*, 1990; Lelieveld and Crutzen, 1991; Saxena and Lin, 1990; Zwodziazk and Zwodziazk, 1990; Warneck, 1991; Mohnen and Vong, 1993; Dentener, 1993; Jonson and Isaksen, 1993; Hallberg *et al.*, 1994; Radojevic *et al.*, 1995; Acker *et al.*, 1995a; Fuzzi, 1995; Xiaohong *et al.*, 1997; Möller *et al.*, 1996a; Choularton *et al.*, 1997; Sedlak *et al.*, 1997). Clouds also play an important role in the removal of trace species in the troposphere via wet deposition (Rodhe and Granat, 1984; DeFelice and Saxena, 1991; Baron and Denning, 1993; Miller *et al.*, 1993; Hansen *et al.*, 1994; Schemenauer *et al.*, 1995; Weathers *et al.*, 1995). Therefore, the chemical composition of atmospheric liquid phase is a sensitive indicator of changing emission patterns.

ANTHROPOGENIC EMISSIONS IN EAST AND WEST GERMANY BEFORE AND AFTER THE UNIFICATION

Table 1 shows clearly that the air pollution above East Germany before 1990 had been dominated by SO₂ and alkaline dust, with enormous levels of emissions compared to West Germany. For NO, the situation was the reverse, with higher emissions in West Germany (Report of the Federal Government, 1997).

The ratio of acidic to alkaline precursors in East Germany was more than 2.5 times higher than in West Germany in 1989. While for 1994 this ratio was in West Germany somewhat lower compared to

Table 1. Emission situation in West and East Germany 1980–1994 (data in kg km⁻² yr⁻¹)

Source	Former West Germany			Former East Germany			
	1980	1989	1994 ^a	1980	1989	1992	1994 ^a
Total SO ₂ emissions	12,726	3789	3515	40,155	48,500	23,613	19,579
Power stations ^b	10,574	2643	2405	28,949	38,013	20,908	17,077
Municipal	1359	547	579	2659	2880	166	148
Other	793	599	531	8547	7607	2539	2354
Total NO emissions (as NO ₂)	10,526	8632	7103	6619	6886	4569	4099
Power stations ^b	4638	2864	2156	4080	4292	2335	1902
Traffic	5140	5261	4356	1652	1735	1855	1846
Municipal	575	426	539	711	637	286	258
Other	173	81	52	176	222	93	93
Total NH ₃ emissions	2301	2236	2083	2428	2419	1098	960
Total dust emissions ^c	2707	1661	1524	17,871	18,711	4052	3462
Acidic precursors (total (SO ₂ + NO ₂) in 10 ³ mol km ⁻² yr ⁻¹)	428	247	209	771	908	468	395
Alkaline precursors (total NH ₃ + 10% of dust ^d 10 ³ mol km ⁻² yr ⁻¹)	142	136	127	188	189	75	65
Acidic/alkaline precursor ratio	3.0	1.8	1.6	4.1	4.8	6.2	6.1

^a Estimated.

^b Heating, electricity production, industrial combustion.

^c The term "dust" refers collectively to all solid components of the atmosphere and can have very varied chemical properties depending on its formation process. Alkaline components of dust influence chemical processes in the atmosphere importantly.

^d Being calcium, assumption based on data given in Mohry and Riedel (1981) and Meyer *et al.* (1996).

1989, it increased strongly in East Germany after the unification. This was mainly due to the rapid decrease of dust (Ca) emissions combined with a substantially lower drop of SO₂ emissions in this region.

Period before unification

The GDR was one of the European countries with highest stress on the environment. This was mainly caused by efforts to approach independence in the energy sector. From 1970 to 1987 the increase in primary energy consumption amounted to 29%. Lignite was the dominant fuel, meeting some 70% of the country's primary energy requirements. Beside high sulphur and ash content of domestic lignite, the high salt content has also contributed to high tropospheric excess chloride. There is only one HCl emission estimate available, given by Möller (1990), being about 90 Kt HCl yr⁻¹. This development and practically complete lack of flue-gas desulphurisation led to a persistent increase in SO₂ emissions, reaching a maximum of almost 48,500 kg km⁻² yr⁻¹ (1989), see Table 1. Nevertheless, emission of dust remained nearly constant due to improved stack-gas filtering and, consequently, dust removal. Contrarily, in West Germany SO₂ emissions decreased in the 1980s, because of complete introduction of flue-gas desulphurisation in 1986. Only in the Buschhaus power plant near the former inner-German border the desulphurisation system became fully operational in the second-half on 1987.

Nitrogen oxides were produced almost exclusively by high-temperature processes, mostly in plants and engines. In the former West Germany emissions increased until 1986; since then, they have been decreasing because of several pollution control measures in large combustion plants. Large differences were (and do still exist) between East and West Germany in NO emissions by traffic, due to differences in the degree of motorisation, type of car fleet and good transportation. More essential, however, for air pollution between both parts of Germany was the ratio between high-stack emissions (large power plants can directly emit into the cloud layer) and ground-based emissions: ~ 0.5 for West and ~ 1.8 for East Germany, respectively. Therefore, the NO emission into higher atmospheric levels, based on per unit area, was by a factor of 1.3 larger in East than in West Germany. Another important pollution source in both parts of Germany is agriculture. From 1970 a permanent increase in the use of nitrogen fertilisers was observed on both sides of the border. Since 1987/1988 it has been decreasing steadily only in West Germany (about 17% in four years).

Period after unification

The sharp decrease of emissions between 1989 and 1991 (Table 1), however, was not caused by air-pollution control management. The only reason was the collapse of nearly the whole industrial and agricultural structure in East Germany, as a result of low

demand of industrial and agricultural products and of energy (primary energy consumption decreased from 1989 to 1991 by 37%, and by a further 10% till 1993; from 1989 to 1993, lignite production decreased by some 62%). Several emitted pollutants like SO₂, NH₃, HCl and dust decreased in the last five years at about 10–20% per year on average. No such rapid decrease has ever been observed in other countries. In the second phase (1992–1994), air-pollution control, such as more efficient removal of dust emission in power plants, use of coal with lower sulphur content and, most recently (1996), installation of flue gas desulphurisation equipment, resulted in a further but not so spectacular emission reduction. On the other hand, the drop of total NO emissions was smaller because the reduction of NO from power plants and industry (in the same order like SO₂ emission) was overlapped by increasing NO from traffic. Between 1990 and 1993, private motor-vehicle transport and transport of goods by road increased rapidly by 16 and 100%, respectively. In the same period the total number of cars in East Germany increased by 27%, trucks and towing vehicles by 133% (in West Germany the increase was only 6% for both types). The amount of livestock in East Germany has reduced drastically since 1990. For example, by 1992 the number of pigs, cattle and poultry decreased by 30–50%. Modest increases in NH₃ emissions due to corrections in agriculture policy, as expected by Friedrich *et al.* (1996), could be possible in East Germany. Recent data show a modest increase in number of poultry and beef cattle (3–10%) from 1992/1993 to 1995 and a slight increase in ammonia deposition in East Germany in 1993 (Kallweit, 1995). In West Germany in that time period animal husbandry remains nearly constant.

EXPERIMENTAL

The precipitation monitoring station Seehausen (21 m asl; 52,40°N; 11,73°E) was operated by IFT Leipzig until 1995; since 1996, BTU Cottbus has been the operator. Wet-only precipitation samplers (Marquardt and Ihle, 1988) are used there for automatic collection of precipitation with a time resolution of 4 h. The Seehausen station lies 100 km north-east of the mountain-site measuring station Mt. Brocken/Harz Mountains (1142 m asl; 51,80° N; 10,67° E), where BTU Cottbus has implemented a cloud chemistry monitoring program. For hourly sampling of cloud water (before 1993 on an event basis) a passive string collector (ASRC design, Mohnen and Kadlec, 1989), installed within an automatic wet-only sampling unit, is used at this site. These short-time resolutions are necessary to resolve the typical time scale of changes in meteorological conditions. Data completeness is about 88% for precipitation and 82% (of frost-free periods only) for clouds. Procedures for storage, transport and analysis of the liquid-phase samples are the same at each site. All samples are stored at 4°C until laboratory analysis within 10 days of sampling. On arrival, the samples are immediately filtered through a 0.45 μm one-way filter and analysed by ion chromatography and for pH and conductivity. The analysis of major components in liquid-phase atmospheric samples is rigorously checked using

ion-balance calculations and by comparing measured and calculated conductivity. The whole measurement and analytical procedure is based on a quality assurance/quality control (QA/QC) program as described in Reports 85 and 102 of the World Meteorological Organisation (WMO, 1992 and 1994). Annual inter-laboratory calibrations are carried out using standard reference samples, organised by the U.S. EPA within the Global Atmospheric Watch Program (Mohnen, 1990; Hunike, 1993). Our data are among the best in this program (Results of, 1997). At the Brocken station measurements of trace gases (O_3 , NO_x , SO_2) are made using commercial automatic analysers. At both stations standard meteorological parameters are also measured. Precipitation amount and cloud-liquid-water content (LWC) are determined to standardise the rain- and cloud-water concentrations. LWC is measured continuously by a particulate volume monitor based on forward light scattering (Gerber, 1984). The volume weighted means are defined as

$$\frac{\sum_i^n (p \times c)}{\sum_i^n p} \quad \text{and} \quad \frac{\sum_i^n (LWC \times c)}{\sum_i^n LWC}$$

respectively, where p is the amount of precipitation and LWC the liquid water content of clouds during the sampling time of the individual sample i , c the concentration for a specific ion of the individual sample i , with a total of n samples available for averaging. The air mass origin for each precipitation and cloud-water sample is classified using 72 h back-trajectories starting at 900 hPa (cloud level). This transport analysis is based on an isotropic (3D-) model of the Meteorological Institute of the Free University of Berlin (Reimer and Scherer, 1991). More detailed descriptions of the location, equipment, measurement parameters, sampling procedure, analytical methods, minimum detection limits, the quality assurance/quality control program and the data interpretation are given in Marquardt and Ihle (1988), Brüggemann and Rolle (1995), Möller *et al.* (1994, 1996a, b, c), Acker *et al.* (1995), Wieprecht *et al.* (1995), Marquardt and Brüggemann (1995), Naumann (1996), Marquardt *et al.* (1996), Acker and Wieprecht (1996).

RESULTS OF THE PRECIPITATION CHEMISTRY

The chemical composition in precipitation may change with time in response to natural and anthropogenic emissions, amounts of chemicals entering the atmosphere, meteorological factors and physical and chemical transformation processes in the atmosphere. Records of the monitoring station Seehausen, with 13 years of continuous data up to the present, have been selected. Methods of collection and analysis have been

kept consistent over time. Trends in annual volume weighted mean-ion concentrations have been investigated (Marquardt and Ihle, 1988). The average rain water chemistry at Seehausen (all entry sectors) before and after 1990 is given in Table 2.

Sulphate clearly dominates. Altogether the figures show the definite decrease for sulphate, calcium, magnesium, chloride and ammonium in the period 1990–1992 in comparison with the period 1983–1989 whereas no changes have been observed for sodium, potassium, nitrate and also H^+ . Examining the data set obtained since 1992 until 1996 for all entry sectors, no definite development (increase or decrease) in annual precipitation weighted concentrations of the rain water components can be established. A high variation in all parameters is observed, also caused by different influence of a number of meteorological factors in the years, for example the amounts of precipitation (Marquardt *et al.*, 1996).

As the aim of this paper is to show differences in composition of precipitation crossing over eastern or western part of Germany before reaching the station Seehausen, the data have been classified concerning different entry sectors, see Fig. 1, by means of back-trajectories. The sectors named “East” and “West” and the selection of these sectors is based on the geographic line to the main industrial areas in East Germany (e.g. industrial centre Halle/Leipzig, brown coal district near Cottbus) and West Germany (e.g. industries in the Ruhr area and south of that; main fuels hard coal and oil, brown coal from Lower Rhine), respectively, and to exclude marine influences. The assignment of these two sectors relative to areas with characteristic emissions (see also Fig. 1) is therefore not identically with the meteorological definition east or west.

In Fig. 2a and b the development in concentrations of sulphate, calcium, nitrate and H^+ in rain water from sectors “East” and “West” are compared. The only significant change in rain water acidity is observed in samples connected with air masses arriving the station Seehausen from sector “East”, see Fig. 2b. Rain from this sector also shows highest concentrations of major ions. The rain water calcium (sector

Table 2. Volume weighted concentrations of dissolved substances in wet only precipitation at the station Seehausen

$\mu\text{eq } \ell^{-1}$	1983–1989 ^a	1990–1992 ^a	1993	1994	1995	1996
SO_4^{2-}	150	82	69	59	59	51
Ca^{2+}	59	39	21	21	37	20
Mg^{2+}	12	8	5	8	10	7
Cl^-	63	47	30	44	41	27
NH_4^+	85	59	55	46	51	61
Na^+	33	34	21	30	40	21
NO_3^-	45	47	44	39	42	48
K^+	6	6	5	4	3	1
H^+	44	42	44	41	25	21
Precipitation mm	526	532	708	698	474	455

^aArithmetic mean of annual volume-weighted values.

“East”) concentration in 1996 has dropped to 14% of the 1989 concentration (Fig. 2a). Decrease of sulphate (sector “East”) concentration is less sharp, and increasingly stagnant since 1993. Therefore, this annually changing acid-base relation explains the dramatic increase in rain water acidity in precipitation derived from sector “East”. The SO_4^{2-} in sector “West” rain water generally follows the West German emission trend. The much higher sulphate concentrations in 1985 and 1986 were caused by emissions of the Buschhaus power plant (see chapter above), which was commissioned in 1985 without a sufficient acting desulphurisation system. The considerable higher nitrate concentration in “East” rain comparing to “West” could be explained by the different emission patterns and the different ratio of high-stack and

ground-based emissions (see section before). The NO_3^- concentration trend in rain from sector “West” follows the West German emission trend. The slight increase of NO_3^- in rain from sector “East” also reflects the emission trend in East Germany until 1989. However, the continuous increase after 1990 of “eastern” nitrate does not comply with the emission figure. Could it be possible that “true” NO emissions in East Germany are higher? Despite lower power plant capacity, the emission factor could have increased (Meyer *et al.*, 1996), however, not yet taken into account in NO emission estimate.

The decline in concentrations of sulphate, calcium, ammonium, chloride observed since 1989 in precipitation from sector “East” is roughly correlated with a similar decline (percentage base) in SO_2 , dust, NH_3 and Cl emissions for East Germany during that period, see Table 3. For the precipitation chemistry as a whole it must be considered that between 5–26% (mean 12.1%) of the annual precipitation amount at the station Seehausen comes from sector “East”, in comparison to 22 and 50% (mean 33.7%) associated with sector “West” (Marquardt *et al.*, 1996). The rate at which East German emissions were dropping has been going decreasing drastically since 1993. This has also led to smoothed precipitation concentration changes as shown in Table 3 and Fig. 2a. With a small delay in time also the trend of acidity increase in sector “East” precipitation seems to be halted in 1995. The value for the H^+ concentration in 1996 is clearly below the 1995 value, see Fig. 2b.

About 40% of all sector “East” events had a transport distance up to 500 km (only within Eastern Germany) 24 h before reaching Seehausen. Fifty percent are connected with larger transport velocities and hence distances up to 1000 km from Seehausen. These events could have polluted air masses from SE Poland and NE Czech Republic. However, the influence from long-range transportation is not so important, compared to the percentage of own sources to the deposition budget. The total sulphur deposition in Eastern Germany in 1993 amounts 470 Kt S whereas Poland and Czech Republic contribute to the total German sulphur deposition with 39 and 81 Kt, respectively (Report of the Federal Government, 1996; Zavodsky and Pukancikova, 1995). Time trends in deposition are generally parallel trends in concentration over the observed period. The development in wet deposition

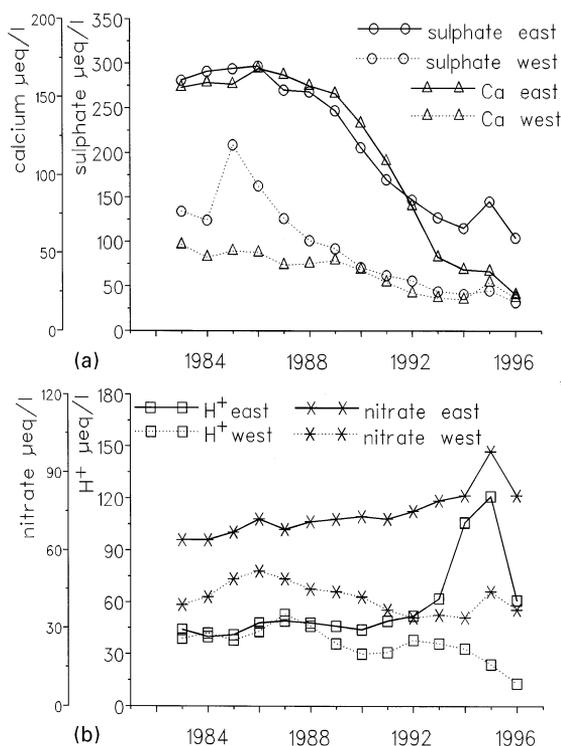


Fig. 2. (a) and (b) Comparison between trends of the concentrations of sulphate, calcium, nitrate and H^+ in Seehausen rainwater from sector “East” and “West”.

Table 3. Percentage decline in emission and precipitation concentration

Components emission/precipitation	Emission East Germany		Precipitation concentration sector “East”, Seehausen	
$\text{SO}_2/\text{SO}_4^{2-}$	1989–1993	– 57%	1989–1993	– 49%
	1993–1994	– 7%	1993–1994	– 10%
$\text{Dust}/\text{Ca}^{2+}$	1989–1993	– 80%	1989–1993	– 69%
	1993–1994	– 8%	1993–1994	– 17%
$\text{NH}_3/\text{NH}_4^+$	1989–1993	– 58%	1989–1993	– 21%
	1993–1994	– 5%	1993–1994	– 10%

of pollutants as a result of the air-quality improvements in East Germany is detailed described in Marquardt *et al.* (1996) and in Kallweit (1995) and not discussed in this paper.

RESULTS OF THE MOUNTAIN CLOUD CHEMISTRY PROGRAM

Due to the high occurrence of clouds (30–50% of time from April to October), the Mt. Brocken summit is an ideal platform for sampling of cloud water. Simulations of surface wind fields in the Harz Mountains for different synoptic situations (Adrian and Fiedler, 1991) showed that the surface wind at the Mt. Brocken summit itself is relatively uninfluenced by the orography and represents the predominant low tropospheric wind (air masses streaming over the mountain top). Gas- and liquid-phase data from Mt. Brocken are therefore representative for the regional air mass pollution situation (Acker and Wieprecht, 1996). The Mt. Brocken station was designed and implemented in 1991, and the first cloud-water results for a whole frost free period (April/May–October/November) were available in 1992. Therefore, the data obtained at the Brocken station are suited to looking for similarities in the development of the cloud chemistry and in emissions during the second phase of emission decrease after the unification (see also chapter above).

In that context at Mt. Brocken we observed a permanent increase in cloud-water acidity between 1992 and 1994, see Table 4. This result was obtained using data of all entry sectors and it was surprising: the average precipitation H^+ from all transport directions at Seehausen did not show any significant tendency (Table 2).

As measures of trends in ion concentrations in cloud water we have used arithmetic averages and volume weighted averages. Arithmetic averages are sensitive to the occurrence of even a few heavily concentrated samples. These samples can be character-

ised by either pollution events or very low liquid cloud water (LWC), see Möller *et al.* (1996a). To exclude the influence of such outliers, weighted averages were used. Such averages correspond to the concentration one would measure in a hypothetical sample obtained with a sampler that is exposed during the whole averaging period (Rodhe and Granat, 1984). We tested and compared both measures. Because of an anti-correlation between ion concentration and liquid water content (collected cloud-water amount) the LWC-weighted average concentration is about 13–37% lower than the unweighted average. The results for the years 1992–1996 are given in Table 4.

There has been an increase of about 250% in the volume-weighted annual H^+ concentration between 1992 and 1994, for the unweighted averages the difference is 320%. Whereas only no further increase could be established in cloud-water acidity in 1995 using arithmetic averages, the cloud-water weighted average for 1995 is substantial below the 1994 value. This is mainly caused by the significant higher cloud water content of the cloud events in 1995 compared with 1994 and, also compared with 1992 and 1993. In 1995 the LWC frequency distribution shows a shift to cloud events with about 20% higher LWC values (Acker and Wieprecht, 1996). Looking at the H^+ averages for 1996, an inverse tendency in cloud-water acidity will be observed after 1994 until now. The frequency distribution of pH-values in the cloud-water samples for the years 1992–1996, given in Fig. 3, reflects the observed development in cloud water pH. Figure 3 clearly shows that the $[H^+]$ increase between 1992 and 1994 can be explained by the drop of cloud events with pH between 5.5 and 6.5, whereas the percentage of events in the more acid region (pH 3.0–4.5) increased. Since 1995 the pH frequency distribution changes *vice versa*: a decreasing number of very acid events and an increase of more alkaline events (about 3% of events with pH > 7.0 in 1996) which explain the stagnant or even decreasing annual mean of H^+ .

Table 4. Annual cloud-water concentrations in $\mu\text{eq l}^{-1}$, given as arithmetic and as liquid water weighted means; LWC in mg m^{-3}

Year <i>n</i>	1992 35		1993 1054		1994 1069		1995 1340		1996 2049	
	Arithm.	LWC-w	Arithm.	LWC-w	Arithm.	LWC-w	Arithm.	LWC-w	Arithm.	LWC-w
Cl^-	93	73	68	51	119	85	110	74	118	75
NO_3^-	365	318	280	192	329	252	364	228	347	248
SO_4^{2-}	288	254	265	189	273	214	320	213	304	227
Na^+	128	76	60	43	117	80	117	76	121	74
K^+	—	—	—	—	12	9	4	2	2	1
NH_4^+	378	333	410	290	394	296	468	297	454	332
Ca^{2+}	133	114	54	33	109	76	62	40	62	38
Mg^{2+}	32	26	26	17	36	25	31	20	28	17
H^+	35	36	83	70	146	126	144	105	106	92
LWC		273		277		309		392		370

As already mentioned, the observed increase in acidity is all the more interesting because the Mt. Brocken cloud water data in Table 4 reflect the atmosphere pollutant loading from all entry sectors. The apparent lack of change in concentrations for the other main ions at the Brocken station does not follow the percentage reduction in pollutant emissions in Germany between 1992–1994. So the correlation coefficients for the linear regression of the sum of the major acid anions SO_4^{2-} and NO_3^- upon H^+ are very low (0.22–0.37). This poor correlation suggests that little of the variability in the annually averaged $[\text{H}^+]$ at Mt. Brocken can be accounted for by variations in the $[\text{SO}_4^{2-}]$ and $[\text{NO}_3^-]$.

Table 5 shows characteristic differences in the mean-ionic concentrations and their standard deviations in clouds collected at Mt. Brocken summit from air masses with entry sector “East” and “West”, respectively. These data indicate that the cloud-water composition is essentially determined by different polluted air masses. At the Brocken station we found significant differences in SO_2 concentration between western and eastern/southeastern air masses. The occurrence of SO_2 pollution episodes (daily averages > 5 ppb) in the measuring period 1992–1995 is 18%. Short-time pollution (several hours) go up to 120 ppb. We found that for 82% of the events with high SO_2 -loading, the air was transported over regions within sector “East”, impressively underlined in Fig. 4 by the relationship between daily SO_2 mixing ratios and the mean wind direction. There are, as already mentioned, the industrial centres of East Germany.

However, back-trajectory calculations show that cloud events from entry sector “East” also could have been influenced from polluted areas in southeastern Poland and northeastern Czech Republic (the so-called Black Triangle). This idea of possible long-range transport (certainly dominant within the cloud layer) is supported by measured SO_2 concentrations in eastern air masses (average 12.1 ppb) that are still 10 times higher than in western air masses Germany

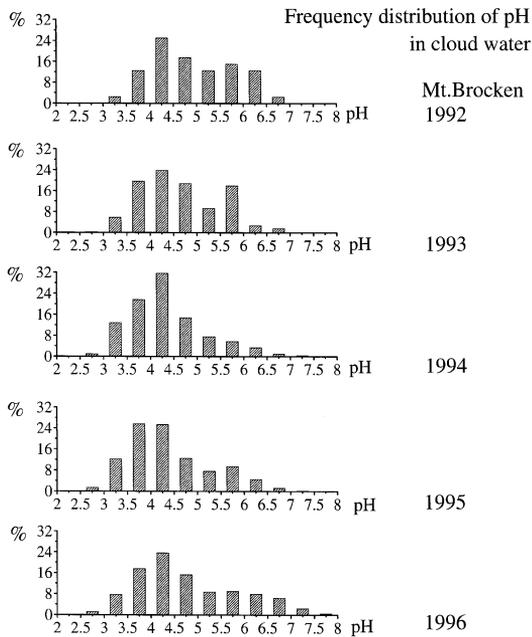


Fig. 3. Frequency distribution of the Mt. Brocken cloud water pH values for the years 1992–1996.

Table 5. Cloud-water composition for different sectors at Mt. Brocken 1993–1994 (in neq m^{-3} air volume)

Species neq m^{-3}	Entry sector “east” $n = 98$ events	Entry sector “west” $n = 401$ events
SO_4^{2-}	142 ± 109	74 ± 17
NO_3^-	119 ± 148	79 ± 20
Cl^-	16 ± 43	21 ± 12
NH_4^+	128 ± 92	113 ± 29
Ca^{2+}	61 ± 121	19 ± 10
H^+	62 ± 47	26 ± 9

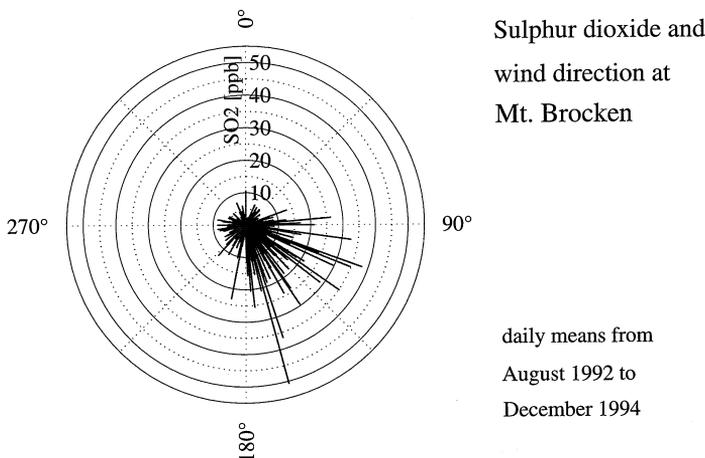


Fig. 4. SO_2 mixing ratios at Mt. Brocken in relation to the wind direction.

(average 1.2 ppb) despite of the drastic decrease in SO₂ emissions in East Germany.

CONCLUSION

In this contribution we have described the evolution of the air-pollution situation in East Germany. We have shown that the chemical composition of rain and cloud water can be a sensitive indicator for changing emission pattern, especially when sector-classified data are used. Our investigations of 13 and 5 year records of precipitation and cloud water chemistry, respectively, are the longest for any site in East Germany and therefore extremely valuable for assessing trends in atmospheric liquid-phase chemistry there. However, we hasten to point out that our observation time is actually quite short on a climatological time scale. Our data provide some insights into identifying trends and assessing variability in long-term series of precipitation and cloud chemistry data. The SO₂ mixing ratio in air masses originating from sector "East" is still 10 times higher than in those from western directions. The observed high increase in atmospheric acidity in cloud water and in sector "East" precipitation samples since 1992 by about 100% per year (with probably impact on ecosystems) seems to have stopped in 1995. The acidity of precipitation from sector "West" has declined slightly recently. A more complex consideration of change in dust composition as a neutralising factor and of the role of aerosols in the cloud formation process is necessary. Because of the high complexity of atmospheric chemistry, long-term measurements are needed to distinguish between the different microphysic, dynamic and air pollution influences on the cloud and rain water quality.

REFERENCES

- Acker, K., Möller, D., Wiprecht, W. and Naumann, St. (1995b) Mt. Brocken, a site for a cloud chemistry measurement programme in Central Europe. *Water, Air and Soil Pollution* **85** (4), 1979–1984.
- Acker, K. and Wiprecht, W. (1996) SANA-Report C1.2 Evaluation of a Cloud Chemistry Model by Measurements at the Brocken station. BTU Cottbus, in German.
- Adrian, G. and Fiedler, F. (1991) Simulation of unstationary wind and temperature fields over complex terrain and comparison with observations. *Beitraege zur Physik Atmosphäre* **64**, 27–48.
- Baron, J. and Denning, A. S. (1993) The influence of mountain meteorology on precipitation chemistry at low and high elevations of the Colorado front range, U.S.A. *Atmospheric Environment* **27**, 2337–2349.
- Brimblecombe, P. (1992) History of atmospheric acidity. In *Atmospheric Acidity-Sources, Consequences and Abatement*, eds M. Radojevic and R. M. Harrison, pp. 267–304. Elsevier, London.
- Brüggemann, E. and Rolle, W. (1995) In *Acid Rain Research: Do we have enough answers?* eds G. J. Heij and J. W. Erisman, pp. 403–406. Elsevier, Amsterdam.
- Chandler, A. S., Choularton, T. W., Dollard, G. J., Gay, M. J., Gallagher, M. W., Hill, T. A., Jones, B. M. R., Penkett, S. A., Tyler, B. J. and Bandy, B. (1989) A field study of the oxidation of SO₂ in a cap cloud at Great Dun Fell. *Quarterly Journal of the R Meteorology Society* **115**, 397–420.
- Choularton, T. W. *et al.* (1997) The Great Dun Fell cloud experiment 1993: an overview. *Atmospheric Environment* **31**, 2393–2405.
- DeFelice, T. P. and Saxena, V. K. (1991) The characterisation of extreme episodes of wet and dry deposition of pollutants on an above cloud-base forest during its growing season. *Journal of Applied Meteorology* **30**, 1548–1561.
- Dentener, F. (1993) Heterogeneous chemistry in the troposphere. Promotion, University Utrecht, ISBN 90-393-0317-7.
- Friedrich, R., Wickert, B. and Laing, R. K. (1996) SANA-report A1.2 Investigation of air pollutant emissions in the New German Federal Länder. University Stuttgart IER, (in German).
- Fuzzi, S. (editor) (1995) *The Kleiner Feldberg Cloud Experiment* 1990. Kluwer Academic Publishers, Dordrecht, The Netherlands.
- Gerber, H. (1984) Liquid water content of fogs and hazes from visible light scattering. *Journal of Climate Applied Meteorology* **23**, 1247–1252.
- Hallberg, A., Noone, K. J., Ogren, J. A. *et al.* (1994) The influence of aerosol particle composition on cloud droplet formation. *Journal of Atmospheric Chemistry* **19**, 153–171.
- Hansen, K., Draaijers, G., Ivens, W. P., Gunderson, P. and van Leeuwen, N. (1994) Concentration variations in rain and canopy throughfall collected sequentially during individual rain events. *Atmospheric Environment* **28**, 3195–3205.
- Hunike, E. T. (1993) Fifteenth analysis on reference precipitation samples by the participating World Meteorological Organisation Laboratories, July 1993. Atmospheric Research and Exposure Assessment Laboratories, U.S. EPA, Research Triangle Park, N.C. 27711.
- Huntzicker, J. J., Cary, R. A. and Ling, C. S. (1980) Neutralisation of sulphuric acid by ammonia. *Environmental Science and Technology* **14**, 819–824.
- Jonson, J. E. and Isaksen, I. S. A. (1993), Tropospheric ozone chemistry. The impact of cloud chemistry. *Journal of Atmospheric Chemistry* **16**, 99–122.
- Kallweit, D. (1995) Deposition Network of the Federal Environmental Agency (UBA)—Results and Trends. In *Acid Rain Research: Do we have enough answers?* eds G. J. Heij and J. W. Erisman, pp. 91–102. Elsevier, Amsterdam.
- Lelieveld, J. and Crutzen, P. J. (1991) The role of clouds in tropospheric photochemistry. *Journal of Atmospheric Chemistry* **12**, 229–268.
- Marquardt, W. and Ihle, P. (1988) Acidic and alkaline precipitation components in the mesoscale range under the aspect of meteorological factors and the emission. *Atmospheric Environment* **22**, 2707–2013.
- Marquardt, W. and Brüggemann, E. (1995) Long-term trends in chemistry of precipitation after longscale transport—effects of atmospheric rehabilitation in East-Germany. *Water, Air and Soil Pollution* **85** (4), 665–670.
- Marquardt, W., Brüggemann, E. and Ihle, P. (1996) Trends in the composition of wet deposition: effects of the atmospheric rehabilitation in East-Germany. *Tellus* **48B**, 361–371.
- Meyer, E., Bischoff, U. and Gräf, H. (1996) SANA-rep. C2.2 Determination of alkaline emission factors at the lignite use in large firing facilities. Institute for Energetic, Leipzig, in German.
- Miller, E. K., Friedland, A. J., Arons, E. A., Mohnen, V. A., Battles, J. J., Panek, J. A., Kadlecck, J. and Johnson, A. H. (1993) Atmospheric deposition to forest along an elevational gradient at Whiteface Mountain, N.Y., U.S.A. *Atmospheric Environment* **27A**, 2121–2136.
- Mohnen, V. A. (principal investigator) *et al.* (1990) An Assessment of atmospheric exposure and deposition to high

- elevation forests in the eastern United States. U.S. EPA, Washington DC 20460, EPA/600/3-90/058.
- Mohnen, V. A. and Vong, R. J. (1993) A climatology of cloud chemistry for the eastern United States derived from the cloud chemistry project. *Environmental Review* **1**, 38–54.
- Mohnen, V. A. and Kadlec, J. A. (1989) Cloud chemistry research at Whiteface Mountain. *Tellus* **41B**, 79–91.
- Möller, D. (1980) Kinetic model of atmospheric SO₂ oxidation based on published data. *Atmospheric Environment*, **14**, 1067–1076.
- Möller, D. (1990) The Na/Cl ratio in rainwater and the seasalt chloride cycle. *Tellus* **42B**, 254–262.
- Möller, D., Acker, K. and Wieprecht, W. (1994) Cloud chemistry at Mt. Brocken/Harz. *Physico-Chemical Behaviour of Air Pollutants*, eds G. Angeletti and G. Restelli, In Report EUR 15609/2 EN, Office for official publ. of the EU, L-2985 Luxembourg, 968–974.
- Möller, D., Acker, K. and Wieprecht, W. (1996a) A relationship between liquid water content and chemical composition of clouds. *Journal of Atmospheric Research* **41**, 321–335.
- Möller, D., Wieprecht, W., Kalaß, D., Acker, K., Auel, R. and Oestreich, A. (1996b) Physico-chemical characteristics of clouds at the Brocken summit. In *Proceedings of EURO-TRAC Symposium 96*, SPB Academic Publishing eds P. M. Borrell *et al.*, Vol. 1, pp. 93–99. Clouds, Aerosols, Modelling and Photo-oxidants.
- Möller, D., Acker, K., Marquardt, W. and Brüggemann, E. (1996c) Precipitation and cloud chemistry in the Neue Bundesländer of Germany in the background of changing emissions. *Idöjaras* **100** (1–3), 117–133.
- Mohry, H. and Riedel, H. G. eds (1981) *Reinhaltung der Luft, Deutscher Verlag für Grundstoffindustrie Leipzig*, 133, in German.
- Munger, J. W. and Eisenreich, S. J. (1983) Continental-scale variations in precipitation chemistry. *Environmental Science and Technology* **17**, 32A–42A.
- Naumann, St. (1996) Relation of physico-chemical properties of clouds at Mt. Brocken (Harz) to transport and different-scale meteorological parameters. Dissertation, Department of Geosciences, Free University Berlin.
- Radojevic, M., Tyler, B. J., Hall, S. and Penderghest, N. (1995) Air oxidation of S(IV) in cloud-water samples. *Water, Air and Soil Pollution* **85** (4), 1985–1990.
- Reimer, E. and Scherer, B. (1991) An operational meteorological diagnostic system for regional airpollution and long term modelling. In: *Proceedings of the 19th ITM on Air Pollution Modelling and its Application in Crete*, Vol. II, 421–428.
- Report of the Federal Government to the Deutscher Bundestag: 6. Air Quality Report of the Federal Government of Germany, 1997, Federal Ministry of Environment, Nature Protection and Reactor Security, Box 120629, 53048 Bonn, Germany.
- Results of the 1996 Global Atmospheric Watch (GAW) Laboratory Intercomparison: (1997) Word Precipitation Center, U.S. Dept of Commerce Contract No. 50EANR500054, (in press).
- Rodhe, H. and Granat, L. (1984) An evaluation of sulphate in European precipitation 1955–1982. *Atmospheric Environment* **18**, 2627–2639.
- Saxena, V. K. and Lin, N.-H. (1990) Cloud chemistry measurements and estimates of acidic deposition on an above cloud base coniferous forest. *Atmospheric Environment* **24A**, 329–352.
- Schemenauer, R. S., Banic, C. M. and Urquizo, N. (1995) High elevation fog and precipitation chemistry in southern Quebec, Canada. *Atmospheric Environment* **29**, 2235–2252.
- Sedlak, D. L., Hoigné, J., David, M. M., Colvile, R. N., Seyffer, E., Acker, K., Wieprecht, W., Lind, J. A. and Fuzzi, S. (1997) The cloudwater chemistry of iron and copper at Great Dun Fell, UK. *Atmospheric Environment* **31**, 2515–2526.
- ten Brink, H. M., Schwartz, S. E. and Daum, D. H. (1987) Efficient scavenging of aerosol sulphate by liquid-water clouds. *Atmospheric Environment* **21**, 2035–2052.
- Walcek, C. J., Stockwell, W. R. and Chang, J. S. (1990) Theoretical estimates of the dynamic, radiative and chemical effects of clouds on tropospheric trace gases. *Atmospheric Research* **25**, 53–69.
- Warneck, P. (1991) Chemical reactions in clouds. *Fresenius Journal of Analytical Chemistry* **340**, 585–590.
- Weathers, K. C., Lovett, G. M. and Likens, G. E. (1995) Cloud deposition to a spruce forest edge. *Atmospheric Environment* **29**, 665–672.
- Wieprecht, W., Möller, D., Acker, K. and Naumann, St. (1995) Influence of cloud physical parameters on chemical composition of clouds. In *Air Pollution III, Air Pollution Engineering and Management*, eds H. Power *et al.*, Vol. 2, pp. 199–205. Computational Mechanics Publications, Southampton, UK.
- WMO-Report 85 (1992) Chemical analysis of precipitation for GAW: laboratory analytical methods and sample collection standards. WMO CH-1211 Geneva 2.
- WMO-Report 102 (1994) Report of the workshop on precipitation chemistry laboratory techniques in Hradec Kralove, Czech Republic, 17–21 October 1994. WMO CH-1211 Geneva 2.
- Xiaohong, L., Mauersberger, G. and Möller, D. (1997) The effects of cloud processes on the tropospheric photochemistry: An improvement of the EURAD model with a coupled gaseous and aqueous chemical mechanism. *Atmospheric Environment* **31**, 3119–3135.
- Zavodsky, D. and Pukancikova, K. (1995) Transboundary transport of acidifying components in Central Europe in 1993, *Acta Meteorological University of Comenianae*, XXIV, 1–13.
- Zwozdziak, J. and Zwozdziak, A. (1990) Atmospheric sulphate formation and air pollution episodes in the upper parts of the Karkonosze mountains, Poland. *Environment Protection Engineering* **16**, 89–98.