

Trends in the composition of wet deposition: effects of the atmospheric rehabilitation in East-Germany

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ABSTRACT

The chemical components in precipitation largely depend on type and quantity of emissions on the course of the air masses at the sampling site. Beginning in 1982, the concentrations of major ions in precipitation at initially 3 sites are described in total as well as arrival sectors. For regions with specific geographical or emission features, 5 to 7 sectors for every sampling site are established, e.g., Scandinavia, or the centres of brown coal combustion in the former GDR. Particularly from the sectors of the former GDR, the precipitation was over-averaged contaminated anthropogenically in the years before the political change. Some components were significantly raised in comparison to other sectors. However, acidity remained on the level of the other sectors in the 80s. In the early 90s, anthropogenic emissions were systematically reduced partly by substitution of brown coal of inferior quality, better flue gas cleaning and partly by closing down industries. The effect of such steps on the wet deposition is being studied in a national German SANA research project (SANA: scientific program of rehabilitation of the atmosphere). In this project, the sampling sites were extended to 7 while maintaining the sampling procedure and the recording of relevant meteorological input-data. As a result, there now exists a homogeneous long-term data base allowing us to study the effects of emissions on wet deposition by the rehabilitation of the atmosphere in the former GDR. The paper focusses on changes in sulphate, nitrate, calcium, acidity, chloride and potassium concentrations in precipitation at the 3 so-called long-term sites. There are conspicuous decreases of some ions on one hand, but there is also an increase of nitrate and acidity, especially in recent years.

1. Introduction

Industrial and natural emissions may travel long distances at cloud level. The chemical components of rainwater thus largely depend on the emissions incorporated in cloudy air masses over areas traversed.

Fundamental changes in the former German Democratic Republic (GDR) after the political change in 1989 included a major effort to reduce the extreme air pollution and led to drastic cuts in emission levels and to considerable industrial

restructuring. The main aims were to investigate: (a) concentrations of major ions in rainwater as a function of emission structures in regions traversed prior to precipitation; (b) deposition including variations in precipitation data; (c) trends in concentration/deposition of pollutants as a whole and for individual arrival sectors in connection with the effects of changes in emission on the deposition of pollutants.

For this purpose, a precipitation sampling network was set up in the former GDR. At 7 sites, sequential samplers operate for 4-h intervals (admitting about 80% of the events), to assign samples to specific arrival sectors. A change in

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emission then directly affects the concentration of chemical components in precipitation, and cause/effect-relations could hence be established.

The stations are Seehausen, Greifswald, Wiesenburg, Angermünde, Artern, Schmücke and Carlsfeld. Sampling at the first 3 began as early as 1982, 1984 and 1988, respectively. The sampling method remained essentially the same for the whole time. The older series can thus be integrated with results obtained from the later SANA project. Comparisons can thus be made with earlier pollutant levels found in precipitation, and quantitative effects of the first changes in emission patterns in the eighties can also be demonstrated.

2. Measuring techniques

2.1. Sampling

The wet-only samplers constructed by the Institut für Energetik (Marquardt et al., 1986) are funnel-shaped with a collecting area of 0.1 m² at a height of 1.6 m and have sequential sample changers; the sampling period amount to 4 h. At temperatures under +3°C, both the funnels and bottles are heated so that solid hydrometeors melt. Three-sided sensors open and close the collecting bottles at the beginning and the end of precipitation. The sensors are automatically heated in 3 stages and therefore dry quickly after rain; the collecting funnel is closed and will not open in the presence of dew or fog.

2.2. Sample handling and analysis

In order to prevent changes between sampling and analysis, the samples were stabilized as described by Brüggemann et. al. (1991). The following components were analysed by ion chromatography: SO₄²⁻, NO₃⁻, Cl⁻, NH₄⁺, Na⁺, K⁺, Ca²⁺, Mg²⁺, besides pH and conductivity.

QA/QC criteria (Topol and Ozdemir, 1986) were routinely observed from sampling through analysis. Samples for which the analysis criteria could not be met were discarded before further data processing (outliers ≈ 5%). With the exception of H⁺, the ion concentrations had distributions which could be approximated well by Gaussian distributions.

Table 1 lists the sites, their coordinates, the commencement of measurements, the number of samples obtained until the end of 1994 (excluding outliers), and the average annual precipitation. Whenever possible, the instruments were set up at stations operated by the German Weather Service, in order to be able to employ the corresponding meteorological data sets. On average, samples were collected from more than 85% of the total precipitation amount, the rest of the events being too small for chemical analyses, lost samples, power failures, and equipment breakdown.

3. Evaluation methods

3.1. General

The amount and composition of precipitation at a particular site essentially depends on the

Table 1. *Geographical situation of the sampling stations, average annual precipitation, commencement of measurements and number of analysed samples, until 1994, without outliers*

Location	Geographical position	Height above sea-level (m)	Average annual precipitation (mm)	Commencement of measurements	No. analysed samples
Greifswald	54° 06'N 12° 24'E	2	580	Jan. 1984	1831
Seehausen	52° 54'N 11° 44'E	21	550	Oct. 1982	2242
Wiesenburg	52° 07'N 12° 27'E	186	649	Jan. 1988	734
Angermünde	53° 02'N 14° 00'E	56	547	Sept. 1991	579
Artern	51° 23'N 11° 18'E	164	469	Sept. 1991	490
Achmücke	50° 39'N 10° 46'E	937	1355	Sept. 1991	1021
Carlsfeld	50° 26'N 12° 36'E	899	1238	March 1993	554

emissions incorporated by air masses. By selecting suitable arrival sectors in terms of geography or similar emission patterns, the effect of specific emission types on the deposition of pollutants can be established (Marquardt and Ihle, 1988; Andresen, 1985; Budd, 1986; Jaffrezo and Colin, 1990). For interpretation of the data of single precipitations, a number of meteorological factors must be taken into account. The concentration of substances in precipitation is calculated in $\mu\text{eq l}^{-1}$. Multiplication by rainfall amount gives the deposition by an individual event of precipitation. The quantity deposited over a certain period is the sum of all individual inputs for an area, mostly given as $\text{meq m}^{-2} \text{yr}^{-1}$.

3.2. Sector analysis

Between 5 and 7 sectors were assigned to each site, depending on their situation relative to areas with characteristic emissions. For example, the sectors of the 3 oldest stations are characterized in Table 2, and shown in Fig. 1 (Seehausen, Greifswald and Carlsfeld). Particular efforts was made to form sectors with emissions from burning brown coal, the primary energy source in the former GDR. Depending on location, this results in sectors of varying width. Wherever possible, extra sectors were defined with industrial conurbations such as the Halle/Leipzig area and Lusatia.

If possible, a distinction was also made between brown coal mining areas in the former GDR and the Czech Republic. Other sectors are: West-Germany, Scandinavia, the North Sea/Norwegian Sea and, if possible, northern and southern Poland (Silesia). Data of the Meteorological Services and later of the Free University Berlin, Institute of Meteorology (Reimer and Scherer, 1991), were used to demarcate arrival areas by 3-dimensional back-trajectory analyses in 1 h steps, starting on site at the 900 hPa-level. Due to possible overlapping of effects from different sectors and distances, the trajectories are limited to 24 h. Definite assignment to sectors was possible in some 80% of all cases, the remainder being situations where an air mass traversed several sectors. These unclear cases were not considered in the sectoral analysis.

3.3. Meteorological parameters

Transport from an emission area to a sampling site is affected by a number of meteorological

factors which may considerably modify the concentrations of pollutants in precipitation. In order to assess their quantitative effects, these factors must be studied separately. For this purpose, some relevant additional parameters (transport velocity, duration of precipitation, duration of dry periods before sampling, type of precipitation, fog during precipitation and season) were also recorded. The first data were grouped into the ranges discussed by Marquardt and Ihle (1988) but not assigned to arrival sectors. Detailed results are planned for publication in a separate paper. Within every meteorologically-modified group, the concentration data between the lowland sites rarely differ by more than 20%.

4. Ion concentrations in precipitation, results and discussion

4.1. Effect of emission areas

Over the measuring period up to 1989, volume-weighted mean ion concentrations were determined at the long-term sites for the sectors defined in subsection 3.2. Figs. 2 and 3 show the results for SO_4^{2-} , Ca^{2+} and H^+ . They illustrate the effects of different emission areas until the political change in East Germany at the end of 1989.

The stations recorded high sulphate levels (up to three times as on average) for sectors whose emissions come mostly from burning brown coal (the former GDR and northern Bohemia). The Halle/Leipzig centre and the brown coal burning area in Lusatia were major contributors. Generally, much less sulphate was found from sectors where the main fuels are oil, natural gas or hard coal, and from Scandinavia.

Elevated calcium concentrations (up to four times as on average) were restricted to areas from the former GDR where the main fuel was brown coal and the flue-gas-cleaning poor. Calcium contributes to neutralizing acidity from the concurrent SO_2 emissions.

The hydrogen ion content was generally found to be higher in samples influenced by emissions from industrial regions, as opposed to the less polluted sectors around the sampling sites, especially from northern directions. Until 1989, H^+ did not rise in direct relation to SO_2 emissions from burning brown coal in the former GDR. Raised

Table 2. Description of sectors for the 3 long-term stations with 4-h sampling protocol

Sector	Area	Emission characteristics
<i>Seehausen</i>		
F	Scandinavia, coast of the ex-GDR	Few industries, main fuel oil and gas
G	Baltic countries/northern Poland	No larger settlements
H	Mainly the former GDR, northern Bohemia, southern Poland	Several conurbations nearby, main fuel brown coal
I	Western Germany south of Ruhr area	Several main fuels hard coal, oil
J	Ruhr area, Belgium	Industrial areas, hard coal, brown coal from Lower Rhine
K	Lower Saxony, Netherlands, southern England	Industrial areas, gas, oil, hard coal
L	North sea, Norwegian Sea, Hamburg, Schleswig-Holstein	Maritime influence prevails
<i>Greifswald</i>		
M	Scandinavia	approx. as sector F but closer to Scandinavia
N	Baltic countries	approx. as sector G but closer to Balticum
O	Central/southern Poland	Silesia hard coal
P	Ex-GDR, northern Bohemia	approx. as sector H, mostly brown coal
Q	Western Germany, southern Lower Saxony, parts of Mecklenburg, Saxony-Anhalt	approx. as sector I+J plus smaller industries
R	Northern Germany, Netherlands, southern England	approx. as sector K
S	North/Norwegian Sea, Denmark	approx. as sector L
<i>Wiesenburg</i>		
11	Northeastern Germany, northern Poland, Baltic, Scandinavia	Brown/hard coal, maritime influence, no conurbation except Berlin
12	Lusatia, southern Poland	Brown coal burning at short distance, hard coal at medium distance
13	The south of the former GDR, northern Bohemia	Brown coal prevails, large conurbations
14	Southern/central western Germany incl. Ruhr area	Hard coal, oil
15	Northwestern Germany, North/Norwegian Sea	Gas/oil, maritime influence

values were not detected because of neutralizing effects of strong concurrent CaO emissions. An acidity increase in precipitation from the former GDR begins after 1991 and increases up to 1994.

4.2. Effects of emission changes

4.2.1. General trends. Emission patterns in Germany have changed over the last decade as a

result of the following developments. (a) Emission control laws adopted in the former West-Germany, named FWG (concerning flue gas desulfurization, nitrogen removal and the use of low-smoke fuels). (b) Plant closures in the FEG (former East-Germany, GDR) and a general substitution of the highly polluting brown coal used before the political changes with less pollution and more efficient energy sources. (c) Improvements

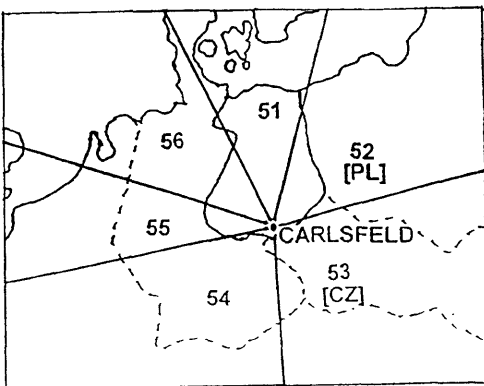
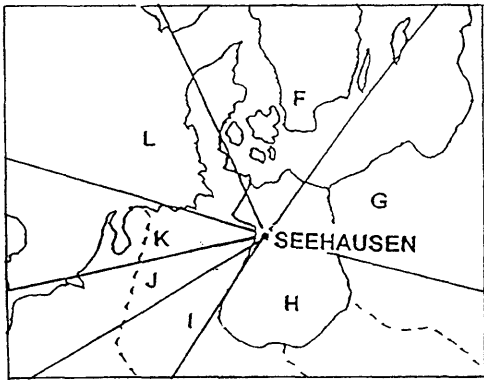
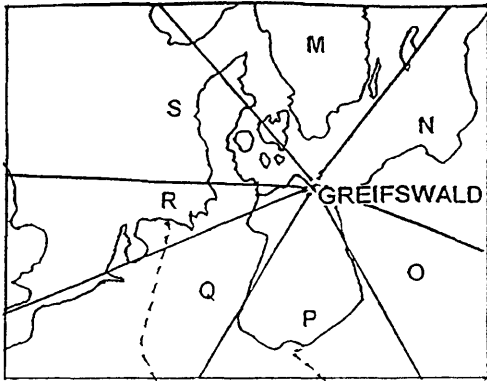


Fig. 1. Arrival sectors of the rainy clouds at Seehausen (F up to L) and Greifswald (M up to S).

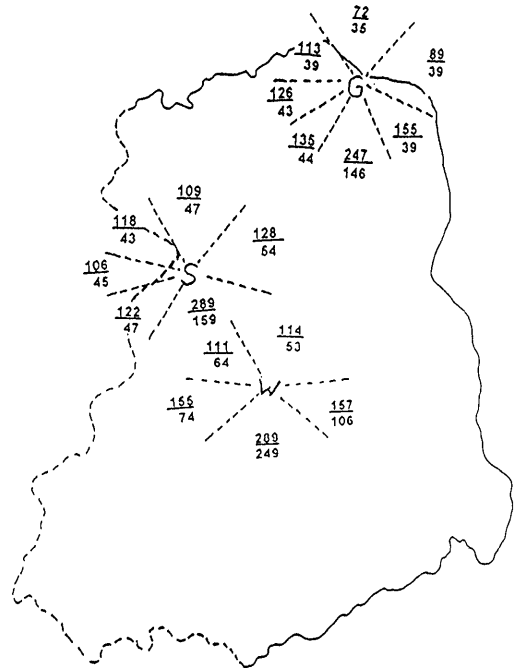


Fig. 2. Sectoral ion concentration ($\mu\text{eq l}^{-1}$) in precipitation until 1989 at Greifswald (G), Seehausen (S) and Wiesenburg (W): value above: sulphate; value below: calcium.

of the flue gas filtration, especially in the FEG. (d) A general increase in car traffic.

4.2.2. Sector — classified trends. (a) Sulphate concentration at Seehausen (sector I). Here the air mass had traversed the Buschhaus power plant near the former inner-German border. This plant was commissioned in 1985 without a sufficient acting desulfurization system but with operational dust extraction facilities. The result was a steep rise (nearly doubling) of the sulphate content in precipitation from arrival sector I (cf. Fig. 4). Transitional measures were implemented step by step, and the desulfurization system became fully operational in the second half of 1987 (reducing the sulphate content in 1988 below the 1984 level). Stricter legislation brought the sulphate concentration down even further.

(b) Sectors from the FEG compared to sectors from FWG. Fig. 5 show the trend in ionic concentrations in precipitation from the FEG at the 3 long-term stations Seehausen, Greifswald and Wiesenburg. The results indicate the following.

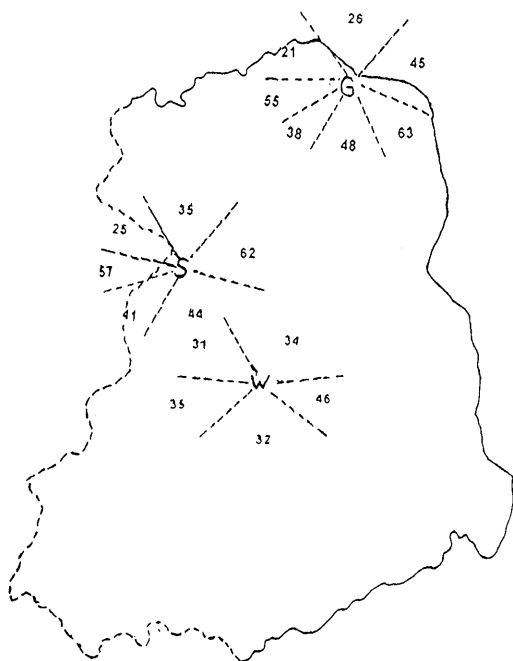


Fig. 3. Sectoral H-concentration ($\mu\text{eq l}^{-1}$) in precipitation until 1989 at Greifswald (G), Seehausen (S) and Wiesenburg (W).

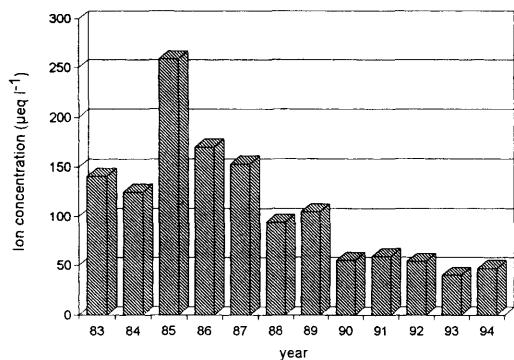


Fig. 4. Trend of sulphate concentration, Seehausen sector "I".

Sulphate. A decrease in the late 80s at Greifswald and Seehausen already began earlier, but in Wiesenburg, only after the political changes. Over the years 1990 and 1992, the decline is greatest, slowing down in 1993. The absolute concentration dropped to about 40% of the base level, but the

values also decreased in the FWG (Table 3) and in Scandinavia (Leck and Rodhe, 1989).

Calcium. The calcium content in precipitation from FEG arrival sectors shows no remarkable modification before the political changes. However, in 1990, a strong decrease commences. The concentration drops to less than 30% in the most recent years. The decrease continues up to the present. In contrast to sulphate, the relation of calcium concentration in the FWG falls only slightly (Table 3). Calcium emissions in the FEG decreased in the nineties by better flue gas cleaning (to >99.9%), and through operating with coal of higher quality and other fuels.

Nitrate. In contrast to sulphate, nitrate concentration increases slightly in clouds crossing the FEG at the end of the 80s; then after the political change, increases more strongly. The ratio FEG to FWG goes up to over 200% (Table 3).

Acidity. The acidity in precipitation crossing the FEG was nearly constant until the political change: At Seehausen and Greifswald, the absolute acidity from both parts of Germany was approximately equally and at Wiesenburg, the precipitation from the FEG was even more basic than from the FWG, indicated by the neutralization effect of the very high calcium content at this site. On the other hand, during recent years, the rapid decrease of calcium content combined with a substantially lower drop of SO_2 emission and simultaneously increasing nitrate concentrations in the FEG, leads to an increasing acidity. At the end of 1994, the precipitation acidity crossing the FEG is 3-fold higher than the precipitation acidity from the FWG.

Chloride. Until 1991, the chloride concentrations in precipitation clouds crossing the FEG was not homogeneous. Then, a clear decrease begins. Only in 1993 did the chloride concentration amount to less than 50% of 1992. In the 80s, the chloride ratio FEG to FWG was nearly 1.8. Now, the same relation is down at 1.1. This decrease is probably caused by elimination of the portions of salt-coal burned, and by the strong reduction of mining and processing of potassium salts in the FEG. This also indicates the trend of potassium.

Potassium. In 1993, the potassium concentration in precipitation decreased by about nearly 50% and ran parallel to the chloride trend.

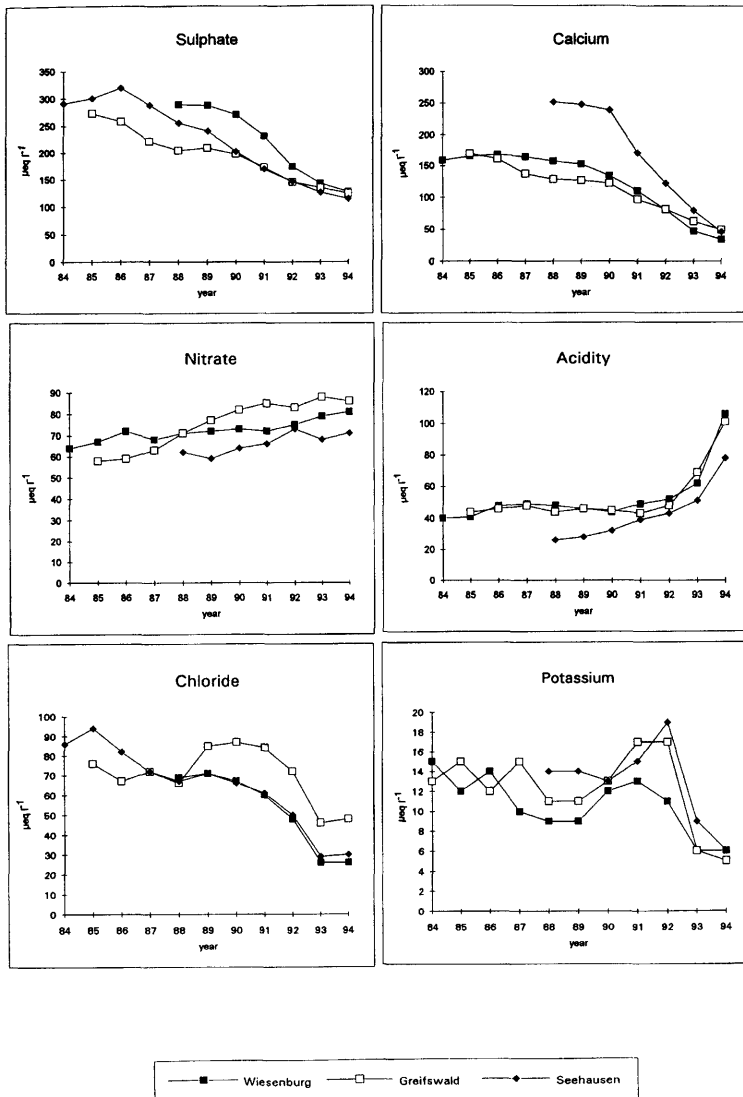


Fig. 5. Trend of some ionic concentrations in precipitation from the FEG (FEG: Former East Germany).

5. Wet deposition

Wet deposition depends on ion concentrations and precipitation amounts during the reference period, with no linear relationship between concentrations and deposited amounts. It is the sum of all deposits from individual precipitation events over a certain period (e.g., a year). At the long-term stations, the variability in precipitation was nearly 300 mm during the studied period (see

Table 4). To identify a trend clearly, one not only needs data on the chemical composition and on the amount of precipitation, but also on the distribution of precipitation over various arrival sectors. That information is listed also in Table 4 and indicates a strong variability found in sectors with strong emissions, e.g., from the FEG (sectors H and P). In particular, this variability amounts to 25.6 to 4.8% (181–21 mm) for sector H (Seehausen), and 20.3 to 4.5% (93–22 mm) for

Table 3. Ion concentrations in precipitation (average of the lowland sites Seehausen and Greifswald) subdivided into sectors FEG (East-) and FWG (West-Germany) in 1985 and 1994; absolute changes in concentrations

	Sector	Concentration ($\mu\text{eq l}^{-1}$)		Change from 1985–1994 ($\mu\text{eq l}^{-1}$)
		1985	1994	
SO_4^{2-}	FEG	298	115	–183
	FWG	124	53	–71
Ca^{2+}	FEG	155	44	–111
	FWG	40	24	–16
NO_3^-	FEG	60	83	+23
	FWG	40	36	–4
H^+	FEG	42	103	+61
	FWG	39	32	–7
Cl^-	FEG	68	33	–35
	FWG	38	29	–9
K^+	FEG	14	6	–8
	FWG	8	5	–3

sector P (Greifswald). If a quantitative assessment is to be made of the effects of emission changes on wet deposition, a breakdown into sectors, is therefore absolutely mandatory.

5.1. Annual wet deposition

Table 5 give the annual deposition data at the 3 long-term stations. The fact that air masses bring different amounts of precipitation from every arrival sector requires further differentiation in the annual amount of depositions.

Table 6 presents the complex connection between precipitation amounts and the total sectoral deposition for some ion types and the FEG and FWG sectors, by comparison of the low precipitation year 1991 and the high precipitation year of 1993. In these years, the sectoral precipitation portion from the FEG is very different, too. Consequently, the table indicates the large absolute and relative differences in deposition which can be caused by the amount of precipitation and the back-trajectory path way. Table 6 demonstrates the importance of precipitation quantity for total sectoral deposition. High concentrations in the samples but low precipitation amounts can lead to clearly lower deposition than reversal conditions. Similar statements are also given in Rodhe and Granat (1984), e.g., for seasonal studies.

6. Conclusions

Research accompanying the current program for atmospheric rehabilitation in the FEG provides a unique opportunity to document the effects of considerable changes in emission patterns on wet deposition both in quantity and quality. At 7 sites, precipitation is collected in 4-h periods. This short-time sampling is mandatory if direct links are to be established between changes in emission in particular areas (for example the FEG) and depositions from precipitation after larger distances. Based on geography and/or emission structure, arrival sectors were identified for each sampling point. In about 80% of all cases, the path of an air mass from which 4-h precipitation samples were taken could be traced back to a particular sector using back trajectories.

Important findings include data on the concentration of major inorganic substances in rainwater, both generally and for rainfall from air masses after traversing specific arrival sectors, and changes during the measuring period. Particular attention is given to data from 3 long-term stations and to depositions originating in the FEG. A comparison with sectors from West-Germany have been carried out, from before and after the political changes.

Clearly, there are some differences between sectors and components. The results also illustrate a

Table 4. Annual % of the precipitation at Seehausen and Greifswald and annual % of the precipitation from the individual sectors

<i>Seehausen</i>								
Year	Total precipitation (mm)	% of precipitation from the individual sectors						
		F	G	H	I	J	K	L
1983	548	6.5	15.4	12.0	16.6	20.0	19.6	9.9
1984	565	7.7	8.6	14.7	17.5	10.8	28.2	12.5
1985	482	3.3	1.1	13.1	10.9	12.5	41.6	17.5
1986	478	6.9	11.1	11.6	9.8	18.2	31.9	10.7
1987	604	8.7	21.1	11.8	6.0	16.2	27.3	8.9
1988	492	7.1	1.9	16.2	20.3	15.0	18.3	21.2
1989	410	11.3	5.3	25.2	19.8	19.1	12.5	6.7
1990	595	9.0	8.2	6.9	20.5	19.9	20.7	14.7
1991	426	10.4	7.0	4.8	21.1	24.8	20.6	11.3
1992	575	9.0	11.5	6.4	31.6	14.3	15.4	11.8
1993	708	3.2	4.3	25.6	28.8	17.8	13.3	7.0
1994	698	3.1	7.6	10.0	19.6	28.4	13.0	18.3
average	550	7.9	9.5	12.1	17.0	16.7	24.3	12.5

<i>Greifswald</i>								
Year	Total precipitation (mm)	% of precipitation from the individual sectors						
		M	N	O	P	Q	R	S
1984	553	13.5	13.8	12.5	6.9	14.3	23.7	15.3
1985	624	7.9	0.9	1.1	4.9	32.5	39.9	12.8
1986	454	17.8	1.2	2.3	20.3	21.6	21.6	15.2
1987	570	15.5	4.3	11.7	13.2	12.2	30.7	12.5
1988	498	6.3	3.0	4.1	6.6	37.5	36.2	6.3
1989	454	18.6	7.2	18.8	10.0	23.0	14.2	8.1
1990	577	6.8	6.1	5.8	11.6	28.5	13.6	27.6
1991	540	14.0	14.4	3.8	4.5	16.0	25.3	22.0
1992	489	11.5	1.3	7.3	4.5	35.0	21.6	18.8
1993	678	12.9	11.4	17.4	11.6	18.8	13.7	14.2
1994	588	8.3	6.6	8.0	8.0	29.7	16.3	22.8
average	580	12.4	5.8	7.3	9.7	24.3	25.1	15.4

complicated non-linear connection between some components. Emission reduction in the FEG does not happen symmetrically for all components, e.g., for SO₂ less than for calcium, superimposed with a slight increase of NO_x emissions. Besides quantitative reductions, qualitative changes of calcium emission also happened in recent years. The com-

bined effects result in a very high increase of acidity in precipitation from sectors in the FEG. However, emission changes do not only happen in the FEG. In the FWG, reductions also occur caused by new regulations, but on a smaller scale. They lead to a slight decrease in acidity. This shows that the level of the different components

Table 5. Annual ion depositions ($\text{meq m}^{-2} \text{ yr}^{-1}$) at Seehausen, Greifswald and Wiesenburg

<i>Seehausen</i>											
	1983	1984	1985	1986	1987	1988	1989	1990	1991	1992	1993
H ⁺	16.9	21.2	11.2	37.8	38.9	23.1	16.7	21.7	16.2	28.5	34.1
SO ₄ ²⁻	68.7	83.8	83.5	85.9	78.0	78.2	68.4	50.5	38.1	40.7	48.1
NO ₃ ⁻	16.3	18.8	23.8	29.5	25.9	23.9	24.1	28.8	21.5	25.2	32.7
NH ₄ ⁺	40.7	46.0	50.2	56.0	50.2	34.0	36.1	40.6	21.2	34.1	46.5
Ca ²⁺	31.1	28.4	27.7	32.8	25.2	34.7	33.3	26.8	18.2	16.2	15.5
Cl ⁻	54.5	30.4	37.5	33.9	23.5	31.9	20.2	33.5	16.0	26.3	16.1
Na ⁺	19.7	16.7	17.5	13.4	11.6	22.6	11.5	17.7	13.4	17.9	11.4
K ⁺	4.6	3.6	4.2	2.8	2.1	3.3	2.1	2.5	3.5	3.5	3.5
Mg ²⁺	7.3	7.2	7.3	6.0	5.2	6.2	5.0	5.6	3.1	4.5	3.9

<i>Greifswald</i>											
	1984	1985	1986	1987	1988	1989	1990	1991	1992	1993	
H ⁺	22.1	23.2	16.8	32.3	26.7	24.4	18.2	24.7	17.3	22.3	
SO ₄ ²⁻	67.7	92.5	70.8	68.5	61.6	65.9	64.9	48.9	38.4	45.8	
NO ₃ ⁻	16.0	25.8	21.0	25.4	20.6	23.6	25.7	29.3	24.7	30.9	
NH ₄ ⁺	45.4	57.4	35.0	46.3	33.6	39.6	46.9	43.6	28.6	37.8	
Ca ²⁺	22.1	23.6	40.4	20.6	19.3	20.6	39.8	24.6	17.2	21.1	
Cl ⁻	27.8	42.5	27.0	23.2	21.0	25.7	46.2	34.7	22.8	22.4	
Na ⁺	17.3	26.6	12.7	11.9	13.4	18.3	25.8	16.5	25.3	17.8	
K ⁺	2.7	4.2	2.2	1.7	1.4	2.5	4.8	5.8	3.6	3.8	
Mg ²⁺	7.3	8.8	6.8	5.0	5.0	6.0	7.6	5.1	5.8	5.6	

<i>Wiesenburg</i>						
	1988	1989	1990	1991	1992	1993
H ⁺	19.7	16.0	26.0	16.6	26.0	27.1
SO ₄ ²⁻	89.1	73.2	98.6	53.7	56.4	60.6
NO ₃ ⁻	25.4	21.2	38.5	23.3	28.3	36.4
NH ₄ ⁺	29.4	28.8	59.6	25.4	36.4	45.9
Ca ²⁺	52.4	46.3	60.5	33.5	23.1	22.2
Cl ⁻	17.4	23.9	38.7	10.7	15.6	16.5
Na ⁺	11.5	10.6	13.3	18.1	16.1	11.0
K ⁺	2.3	2.6	13.3	5.5	4.6	3.6
Mg ²⁺	7.5	6.9	9.0	2.5	5.2	4.4

in rainwater and their different changes in relation to each other, are very important. Further studies on quantitative interactions between emissions of different components and concentrations in precipitation and wet deposition, are necessary.

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Table 6. Comparison of ion concentrations, depositions and rainfall in the 2 meteorologically very different years 1991 and 1993; total values and portions from the FEG

	1991				1993			
annual precipitation	426 mm				708 mm			
portion from FEG	4.8%				25.6%			
precipitation from FEG	21 mm				181 mm			
	SO ₄ ²⁻	NO ₃ ⁻	H ⁺	Ca ²⁺	SO ₄ ²⁻	NO ₃ ⁻	H ⁺	Ca ²⁺
ionic concentration (µeq l ⁻¹) from FEG	170	74	49	109	145	83	62	46
deposition (meq m ⁻²) from FEG	3.6	1.6	1.03	2.3	26.3	15.0	11.2	8.3
total annual deposition (meq m ⁻²)	38.1	21.5	16.1	18.2	48.1	32.7	34.1	18.5
portion from FEG	~9.5%	~7.5%	~6.5%	~13%	~55%	~46%	~33%	~45%

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REFERENCES

- Andresen J. 1985. Modelling of sulfur dioxide emissions and acid precipitation at mesoscale distances. *JAPCA* **35**, 1159–1163.
- Brüggemann E., Gnauk Th. and Rolle W. 1991. Stabilitätsverhalten von ausgewählten anorganischen Spurenstoffen in Niederschlagsproben. *Umweltwissenschaften und Schadstoff-Forschung, Zeitschr. für Umweltchemie und Ökotoxikologie* **3**, 260–265.
- Budd W. W. 1986. Trajectory analysis of acid deposition data from the New Jersey. *Atmospheric Environment* **20**, 2301–2306.
- Jaffrezo J. L. and Colin J. L. 1990. Some physical factors influencing scavenging ratios. *Atmospheric Environment* **24**, 3073–3083.
- Leck C. and Rodhe, H. 1989. On the relation between anthropogenic SO₂ emissions and concentration of sulfate in air and precipitation. *Atmospheric Environment* **23**, 959–966.
- Marquardt W., Ihle P. and Kappe W. 1986. Automatischer großflächiger Niederschlagssammler für Spurenstoffanalysen. *Chemische Technik* **38**, 262–263.
- Marquardt W. and Ihle P. 1988. Acid and alkaline precipitation components in the mesoscale range under the aspect of meteorological factors and the emissions. *Atmospheric Environment* **22**, 2707–2713.
- Reimer, E. and Scherer, B. 1991. An operational meteorological diagnostic system for regional air pollution and long-term modelling In: Proc. 19th ITM on Air pollution modelling and its applications, Crete, 1991, vol II, pp. 421–428.
- Rodhe, H. and Granat L. 1984. An evaluation of sulfate in European precipitation 1955–1982. *Atmospheric Environment* **18**, 2627–2639.
- Topol, L. E. and Ozdemir, S. 1986. *Operations and maintenance manual precipitation measurements systems*. US Environmental Protection Agency, Research Triangle Part., NC.