

Trends of pollution in rain over East Germany caused by changing emissions

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ABSTRACT

Large changes in emissions also cause a significant change in pollutant concentrations in rain water. The influence of these changes on pollutant concentrations in rain water and wet deposition were investigated in different regions and time periods from 1983 to 1999 in East Germany. Initially, this period is characterized by large emissions of SO₂ (about 5400 kt a⁻¹), NO_x (about 750 kt a⁻¹), and dust (about 2000 kt a⁻¹) at the end of the 1980s. After the reunification of Germany in 1990 and restructuring of industry and agriculture, emissions drastically decreased. For example, from 1990 to 1998 in Saxony emissions of SO₂, NO_x and dust decreased by 84, 44 and 97%, respectively. Alkaline components also strongly decreased through efficient dust removal, while no desulphurization was used in flue gases of power and heating plants. As a consequence, the mean acidity of precipitation strongly rose by a factor of three from before 1990 up to 1995 (the mean pH value in 1995 was about 3.9, with minimum values down to 3.6). In 1996 desulphurization techniques were established in power plants and resulted in an increase of pH values to the level in the period from 1983 to 1989/1990. The results for ionic composition (Cl⁻, NO₃⁻, SO₄²⁻, Na⁺, NH₄⁺, K⁺, Ca²⁺, and Mg²⁺, the pH value (acidity), and conductivity) are based on precipitation samples collected in periods ≤4 h. The data were classified with backward trajectories and entry sectors which are characterized by similar emissions and/or geographical regions.

1. Introduction

Natural and anthropogenic pollutants can be transported many hundreds of kilometres downwind from their sources before they are deposited either wet or dry on to the earth's surface. The deposition of atmospheric components can affect terrestrial and aquatic ecosystems (forest decline, lake and soil acidification and/or eutrophication) and cause deterioration of ancient monuments (cf. Marquardt et al., 1988 and 1996a; Likens, 1989; Okochi et al., 2000).

The concentration of pollutants in precipitation is dependent on the pattern and amount of emissions incorporated in the crossing air masses and is also a function of meteorological conditions such as precipitation rate. Large changes in emissions can cause a significant change in the concentrations of pollutants in precipitation. These changes in concentration of pollutants in rain water and wet deposition were investigated in different regions from 1983 to 1999 in East Germany.

During this period substantial changes in emission pattern in the former GDR (here East Germany), Czech Republic and Poland occurred in a short period of time. Emissions before the

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reunification (of the former GDR and the former FRG, here West Germany) in 1990 were characterized by high amounts of SO_2 , NO_x , NH_3 , and dust in the East. After reunification the emission fluxes of these components changed substantially, as a result of changes in industry and agriculture and a drastic increase in traffic. These changes include the shutdown of industrial plants, a reduction of agricultural activity, a decrease of lignite-burning power plants, the substitution of lignite by other fuels (especially oil and natural gas), and a better removal of dust from flue gases. All these changes lead to both positive and negative (e.g., acidification of rain water and in consequence of soil and lakes) consequences (Friedrich et al., 1996; Möller et al., 1996; Marquardt et al., 1996a, 1996b; Brüggemann and Rolle, 1998; Acker et al., 1998; Brüggemann and Spindler, 1999). Since 1996 the flue gas desulphurization technique has been mandatory for all power and heating plants in East Germany. This has changed the composition of precipitation on a large scale as will be examined below.

2. Experimental

The experimental method is based on collecting precipitation samples during periods ≤ 4 h and tracking raining air masses over 24 h by three-dimensional backward trajectories starting at the 900 hPa level, calculated in 1 h steps after Reimer and Scherer (1992). The trajectories are limited to 24 h to prevent possible overlapping of effects from different sectors and the influence of changing meteorological factors.

Precipitation samples were collected at stations of the German Weather Service. The present paper discusses precipitation measurements at the station Seehausen/Altmark (nearly 3300 samples) for the period October 1982 to December 1999. Thus, the data set covering over 17 years in Seehausen is the longest uninterrupted time series regarding short time collection and evaluation by backward trajectories. Furthermore, data from the sampling site Carlsfeld/Westerzgebirge (from March 1993 to December 1999, 2400 samples) are included (cf. Fig. 1). Seehausen (location $11^\circ 44' \text{E}$, $52^\circ 24' \text{N}$, 21 m asl) and Carlsfeld (location $12^\circ 36' \text{E}$, $52^\circ 24' \text{N}$, 899 m asl) are situated in rural regions. Measurements of rain water at other sites are



Fig. 1. Location of the measurement sites Seehausen and Carlsfeld in East Germany.

discussed by Marquardt et al. (1996), Brüggemann and Rolle (1998), and Marquardt and Brüggemann (2000).

All sampling sites had automatic wet-only collectors (applying a sensor inclined to three directions, with an automatic changing device for the sampling bottles which can freely be selected, here 4 h) which were developed and constructed at the Institute of Energetics in Leipzig (Marquardt et al., 1986; Marquardt and Ihle, 1988). The collector was tested in international (by the Swedish Environmental Protection Agency Atmospheric Research Division in Aspvreten, 1987 and 1988) and national (by Umweltbundesamt Deutschland in Deuselbach, 1991 and 1992) comparisons. In the precipitation eight main components, chloride (Cl^-), nitrate (NO_3^-), sulphate (SO_4^{2-}), sodium (Na^+), ammonium (NH_4^+), potassium (K^+), calcium (Ca^{2+}), and magnesium (Mg^{2+}), were analysed by ion chromatography (Metrohm System, Switzerland, conductivity detection and non-suppressed). Acidity (pH-value), conductivity, and meteorological parameters (such as precipitation amount, type and duration, dry periods, wind direction and velocity, and fog) were also registered. The data capture rate for rain events was 85%. Omission of samples was caused by defects in the collector, amounts of precipitation that were too small to analyse for all compounds, and losses of samples on mailing. Silver chloride powder was added to the sample bottles to prevent losses of rain water components through microbiological

activities. The precipitation samples were stored at 4 °C in a refrigerator in the dark prior to postal shipment to the laboratory for analysis. The samples in the parcels were cooled by cool-packs during transport. All components were analysed immediately upon arrival of the samples at the laboratory. Data quality was assessed by an ion balance and conductivity check for each sample. Further quality control was given through participation in international ring analysis by WMO-EPA each year. A detailed description is given by Brüggemann et al. (1995, 1998).

Starting from the collection site, so-called entry sectors (in German "Einzugssektoren", EzS) of air parcels with precipitating clouds were defined, in which regions with similar emission or specific geographical characteristics are summarized. These entry sectors of different sizes (seven for Seehausen and six for Carlsfeld) were selected such that industrial centres in East Germany (EG), Poland, the Czech Republic (CZ) and also relatively clean regions in West Germany (WG) could be distinguished (Marquardt and Ihle, 1988; Marquardt et al., 1996b). The sectors discussed in this article are (cf. Fig. 2):

- the main emission areas of East Germany – sectors H (Seehausen) and 51 (Carlsfeld), with strong emissions from lignite combustions,
- Czech Republic/North Bohemian industrial region – sector 53 (Carlsfeld), also with strong emissions from lignite combustion,

- West Germany – sectors I + J (Seehausen) and 54 (Carlsfeld), with dominating emissions from the combustion of oil, gas, and partly lignite and hard coal.

In the other entry sectors mixed emission conditions often prevailed, and therefore no detailed interpretation was performed in this study. Samples of rain clouds crossing several EzS were also excluded (~20%).

3. Results and trend analysis

3.1. Sampling periods and emission conditions

3.1.1. 1983–1989. This period covers the time before the unification of Germany and the reorganization in the other countries of Eastern Europe. Power, heating and other industrial plants emitted very high quantities of SO₂, NO_x and other waste gases as major acidifiers of precipitation (Huntzicker et al., 1980), and also enormous quantities of industrial dust. This dust in part compensated the acidity of rain by alkaline components such as CaO emitted during lignite burning, as fly ash from sulphur-rich lignite on average contains 15–25% CaO (Schulz and Friedrich, 1967; Friedrich, 1968). Ammonium is the other main alkaline component in rain water emitted as ammonia mainly by agriculture (Munger and Eisenreich, 1983; Casado et al., 1992; Buijsman et al., 1987; Asman et al., 1992; Sutton et al., 1999).

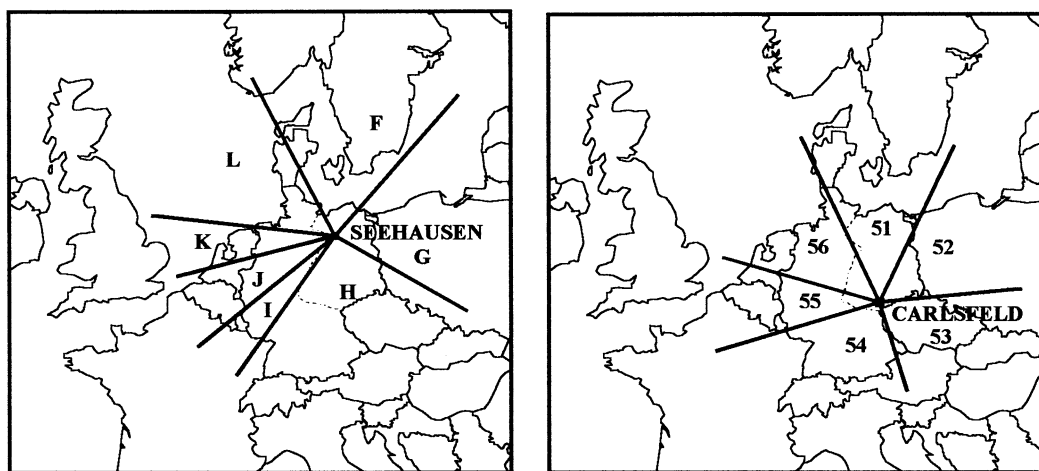


Fig. 2. Entry sectors of the rain clouds at Seehausen (F to L) and Carlsfeld (51 to 56), (-----) old GDR-FRG border.

The emission situation before reunification is shown in Fig. 3 for the former GDR and FRG beginning in 1970 (Federal Government, 1997). While in the former GDR emissions increased (SO_2 from about 4 to 5.4 Mt a^{-1} , NO_x from about 640 to 750 kt a^{-1} , NH_3 from about 220 to 260 kt a^{-1} , and dust with stable emissions of about 2 Mt a^{-1}), in the former FRG emissions decreased (SO_2 from about 3.7 to 0.95 Mt a^{-1} , dust from about 1.3 to 0.41 Mt a^{-1} , and NO_x stable at about 2 Mt a^{-1}), although NH_3 also increased (from about 520 to 560 kt a^{-1}) in the period 1970–1989.

For this period the present investigation intends to clarify whether the mixture of these large emissions from the GDR could have caused extreme acid rain in distant regions.

3.1.2. 1990–1995. The rainwater investigations were continued inside the German project SANA (Wissenschaftliches Begleitprogramm zur Sanierung der Atmosphäre über den neuen Bundesländern/Scientific programme for recovery of the atmosphere). The research goal of the SANA project was to observe and characterize the effects of changes in emissions resulting from reunification in East Germany on the chemical composition of the atmospheric multiphase system and the resulting impact on affected ecosystems.

The period 1990–1995 was characterized by a

restructuring of industry, a reduction of stock farming and a reduction in the numbers of animals, and a drastic increase in traffic by a factor of ~ 1.5 . The number of passenger cars increased from 4.817 to 6.465 millions and of motor lorries from 264 400 to 459 900 in the period from 1990 to 1994 (cf. Gantz, 1993). The traffic emission pattern also changed due to a change from two-stroke to four-stroke engines in East Germany. The worst industrial sources were shut down, waste gas cleaning was improved strongly, and fuels with high contents of sulphur, chlorine, and non-combustible components were substituted by other sources of energy (e.g., oil and natural gas). The flue gas desulphurization technique was only partly established. As a consequence, the basic components of emissions were reduced more than the acidic ones.

The emissions of SO_2 , NO_x , NH_3 , and dust were dramatically reduced in a short time in the former GDR and more slowly in the former FRG, and also in western parts of Europe (cf. Fig. 3).

3.1.3. 1996–1999. During this period the investigations were supported within the national project OMKAS, a research project in the Black Triangle which is the industrial region between South Saxonia (Germany), Silesia (Poland), and North Bohemia (Czech Republic). The emission trends

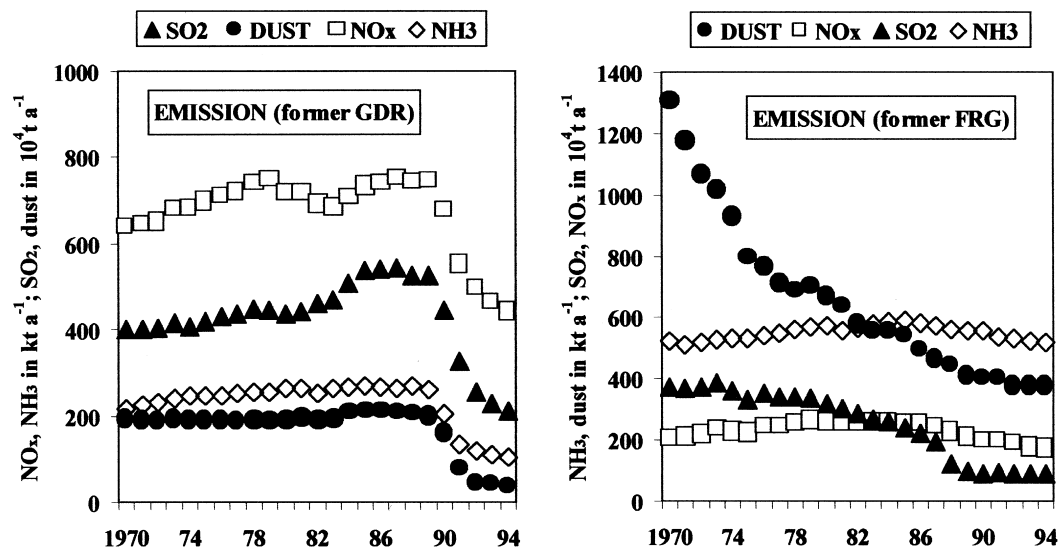


Fig. 3. Annual variation of emissions in former GDR and FRG (Federal Government, 1997).

in the Black Triangle region during the period 1989–1997 are shown in Fig. 4. The reduction of SO_2 , NO_x , and dust emissions is large in the three border regions but also varies. From 1990 to 1998 the emissions in the region of Saxony, the Czech Republic, and Poland decreased for SO_2 to 4, 16, and 62%, for NO_x to 53, 40, and 15%, and for dust to 3, 8, and 13%, respectively (Zimmermann and Bothmer, 2000).

For this period, the study addresses the questions:

- How, when, and in which proportion did the acidification of precipitation after 1995 decrease?
- What are the regional effects of different qualitative and quantitative industrial restructuring

programmes leading to emission reductions in the adjacent countries?

- Are there differences between the effects at low elevation (Seehausen, 21 m asl) and high elevation areas (Carlsfeld, 899 m asl)?

3.2. Trends of pollutants in precipitation

3.2.1. Before 1990. The emission situation in East Germany and other countries in East Europe was characterized by combustion of low-quality lignite with high sulphur and/or salt and ash contents. Dust removal was generally negligible and no flue gas desulphurization took place. The mean annual sulphate concentration in rain water from clouds which had crossed the emission region of East Germany (EzS H, Seehausen) was nearly

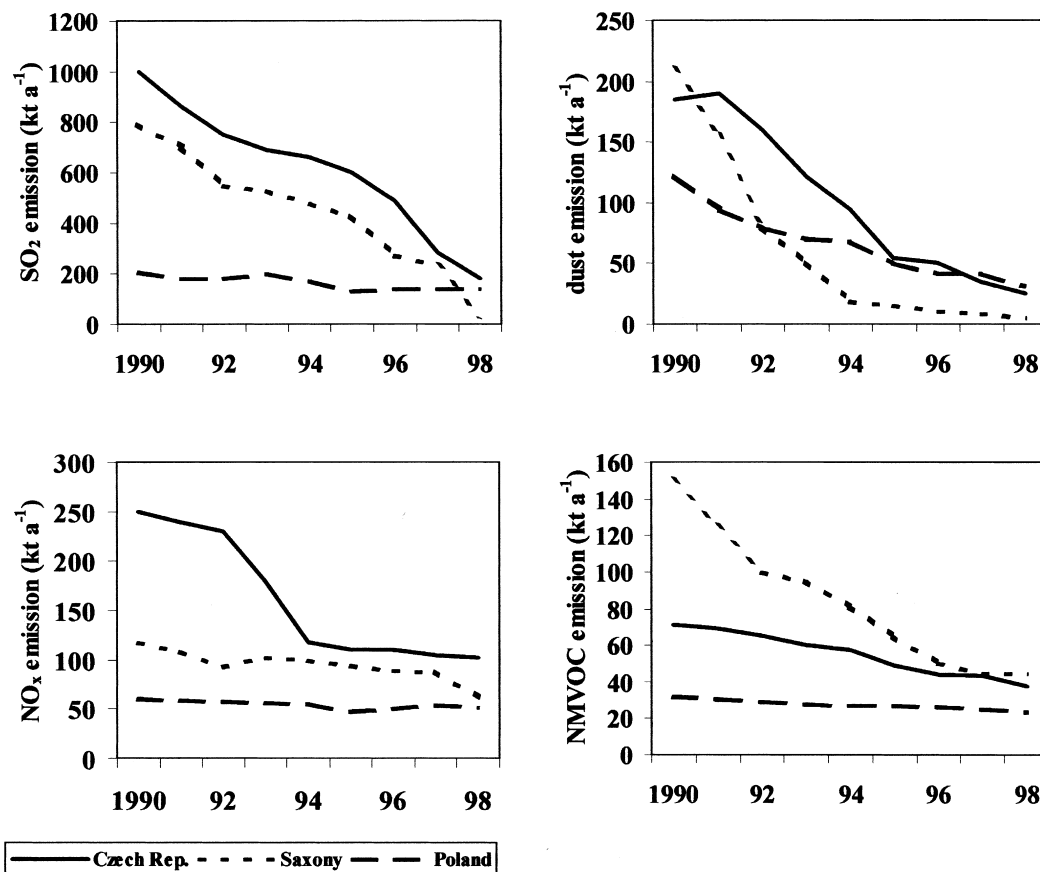


Fig. 4. Annual variation of emissions from Silesia (Poland), Northbohemia (Czech Republic), and Saxony (East Germany) in the Black Triangle (Zimmermann and Bothmer, 2000).

twice as high as in rain from the emission region of West Germany (EzS I + J, Seehausen). The maximum concentration of sulphate and ammonium in 1985/1986 from sector I + J is caused by the Buschhaus power plant near the former GDR–FRG border on the western side (cf. Table 1 and Fig. 5) situated about 90 km SSW from Seehausen (in the entry sector I + J) in a rural region. This lignite-burning plant was established in 1985 without sufficient desulphurization of flue gas but with dust removal (no increase in calcium). The result was nearly a doubling of sulphate content and an increase of ammonium in precipitation from EzS I + J. The ratio of acidic and alkaline components strongly increased (cf. Fig. 8).

In 1987 the desulphurization system at Buschhaus became fully operational and the sulphate, ammonium and acidity content decreased to about the former level.

Calcium is a main trace constituent (partly with higher concentration in rain water than ammonium) of precipitation from the East Germany sector, as the flue ash could contain at most up to 30% CaO. The Ca concentration was higher than in the West Germany sector by a factor of three. The sites in East Germany were more strongly influenced by alkaline emissions, which are generally deposited close to the sources. Hence, at greater distances the ratios between acidic and alkaline compounds will increase. Thus the ratio

Table 1. Annual average volume-weighted concentration for all measured components in $\mu\text{eq L}^{-1}$ for the EzS H (East Germany) and I + J (West Germany) in Seehausen

EzS	Year	<i>n</i>	H ⁺	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	NH ₄ ⁺	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺
H	1983	14	41	78	281	64	153	38	14	156	22
	1984	28	41	87	291	64	158	42	15	159	27
	1985	19	40	93	294	67	178	21	11	156	23
	1986	28	47	90	297	72	179	34	14	168	23
	1987	26	52	81	270	68	142	31	9	164	19
	1988	30	46	72	268	71	129	56	9	157	23
	1989	25	48	75	247	72	136	18	8	152	17
	1990	22	41	73	206	73	140	26	12	133	17
	1991	6	45	68	170	72	130	52	23	109	7
	1992	10	46	53	147	75	112	32	9	80	13
	1993	28	69	25	127	79	107	11	6	47	6
	1994	21	102	33	115	81	96	13	5	39	7
	1995	14	120	26	145	98	106	17	6	45	9
	1996	13	61	15	104	81	97	19	1	32	6
	1997	14	47	20	106	67	105	19	1	34	11
	1998	28	29	31	92	66	92	13	1	41	7
	1999	21	29	30	75	68	81	11	2	42	7
I + J	1983	31	44	59	134	39	81	24	5	55	10
	1984	33	37	44	121	42	88	15	4	47	9
	1985	34	27	61	209	49	105	21	11	51	12
	1986	61	54	44	163	52	102	15	4	50	8
	1987	42	53	45	126	49	84	15	3	42	7
	1988	41	41	46	101	45	70	22	3	43	6
	1989	39	33	46	92	44	64	23	4	45	10
	1990	48	30	37	71	42	60	12	4	39	6
	1991	28	28	29	62	37	56	24	3	31	4
	1992	65	40	31	56	34	50	29	4	24	4
	1993	74	35	26	44	35	44	10	4	21	3
	1994	87	32	27	41	34	39	16	3	20	4
	1995	40	24	18	45	44	41	23	2	31	7
	1996	43	13	22	32	37	43	13	2	12	5
	1997	59	9	23	38	36	52	20	2	19	6
	1998	95	7	21	33	31	39	11	2	17	3
	1999	57	9	11	22	27	30	6	2	10	3

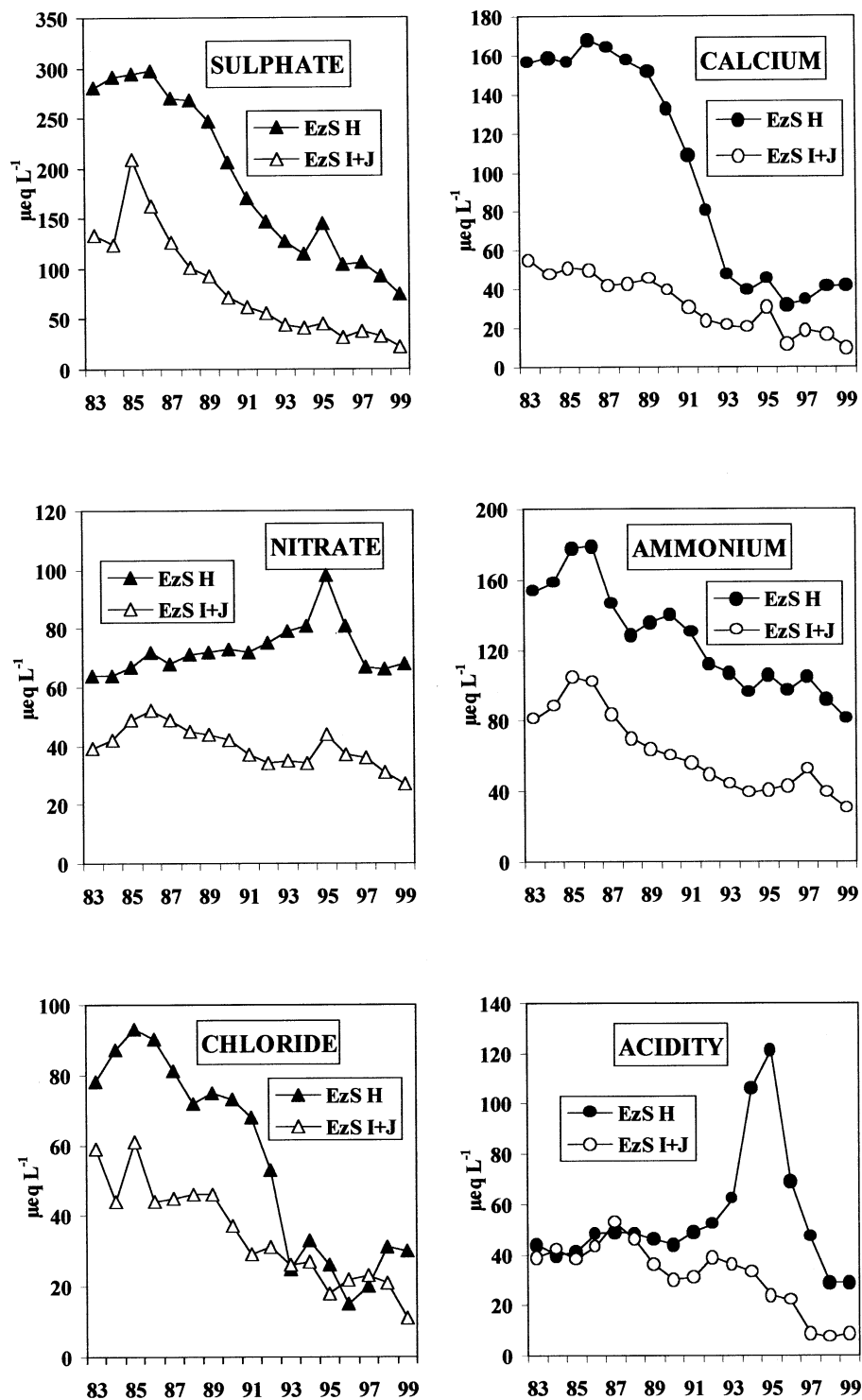


Fig. 5. Annual average volume-weighted concentration of sulphate, nitrate, chloride, calcium, ammonium, and the acidity in precipitation in Seehausen for EzS H (East Germany) and I + J (West Germany).

($\text{SO}_4^{2-} + \text{NO}_3^-$)/(Ca^{2+}) of component concentrations in rain water ($\mu\text{eq L}^{-1}$) for the East German sectors Wiesenburg ($12^\circ 27' \text{E}$, $52^\circ 07' \text{N}$, in the middle of East Germany), Seehausen ($11^\circ 44' \text{E}$, $52^\circ 24' \text{N}$, northwest from Wiesenburg), and Greifswald ($13^\circ 24' \text{E}$, $54^\circ 06' \text{N}$, at the Baltic Sea) was found to be 2.2, 3.1, and 3.5 from 1983 to 1990 on average (Marquardt et al., 1995, 1996). Acidity in precipitation from East Germany and West Germany in this measuring period showed about the same value (pH 4.4–4.5, cf. Fig. 5). As a result, no excessive transport of acidity in cloudy air masses occurred from East Germany to other directions.

3.2.2. 1990–1995. In this period the abovementioned changes in industry and agriculture in East Germany began and continued. The concentration of calcium in precipitation decreased to less than a third within four years and the content of sulphate declined by about 50%. The trend in decreased sulphate and calcium concentration reveals the same trend as the decreased emissions of precursors (cf. Fig. 6). The nitrate concentration increased slightly with a maximum in 1995 and then decreased to the same level as before 1990, probably caused by changes in the oxidizing capacity of the troposphere. The emissions of SO_2 strongly decreased, but only slightly for NO_x , for which industrial emissions decreased and traffic emissions increased. Finally, NMVOC emissions significantly decreased (cf. Fig. 4). The annual mean concentration of SO_2 rapidly decreased (1992, 21 ppb and 1995, 6 ppb at the Melpitz site in northwest Saxony, cf. Brüggemann and

Spindler, 1999), so that tropospheric oxidizing capacity possibly became available for more effective NO_x oxidation. The NO_2 concentration (also in Melpitz) was found to be relatively stable up to 1994, with a maximum in 1995, followed by a decrease (Spindler, personal communication). The simultaneous decrease of NMHC concentration (Gnauk and Rolle, 1998) could lead to a decreased oxidation capacity of the atmosphere by decreased ozone, followed by OH production and hence decreased nitrate production. This effect seems to overwhelm the decreased consumption of OH by decreased NMHC. Currently, this interpretation remains qualitative and needs to be substantiated by modelling calculations.

As salt-rich lignite was no longer combusted the rainwater chloride concentration fell to less than a third by 1993. The very good correlation of calcium with chloride is a hint at lignite burning, because sea salt influence on rain water concentration from sector 51 (Carlsfeld) is negligible and the other sectors have none at all. Ammonium and magnesium contents (the latter not shown here) dropped only by a limited amount. The main alkaline component in rain water is ammonium, with twice the concentrations of calcium at the end of this time period (cf. Figs. 5, 7 and Table 1).

The developments of different precipitation components led to a remarkable result: the acidity of rain water from the EzS H and EzS 51 (East Germany) increased by a factor of about five. This did not occur in the sectors I+J and 54 (West Germany). The annual average pH-value decreased to 3.9 or $[\text{H}^+]$ increased to $120 \mu\text{eq L}^{-1}$. Individual events exceeded $250 \mu\text{eq L}^{-1}$ (in rain water events with minimum 0.5 mm and maximum 3.1 mm precipitation) for sector 51 (Carlsfeld) and the maximum value was $427 \mu\text{eq L}^{-1}$ (in 2.7 mm precipitation) for sector H (Seehausen). The concentration ratio ($\mu\text{eq L}^{-1}$) of the main acidic ($\text{SO}_4^{2-} + \text{NO}_3^-$) and alkaline ($\text{NH}_4^+ + \text{Ca}^{2+}$) components showed the same trend as acidity. This ratio was strongly deferred in the direction of acidic components from 1993 to 1996 (cf. Figs. 5 and 8). In this period it was appropriate to speak of Acid Rain from East Germany (Marquardt et al., 1996a).

The maximum sulphate and calcium concentration from entry sector East Germany (EzS H) in 1995 coincided with the combustion of old stocks

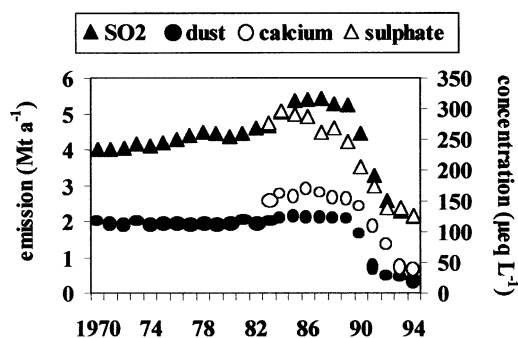


Fig. 6. Annual trend of emissions of SO_2 and dust of East Germany and annual average concentrations of sulphate and calcium of EzS H (East Germany).

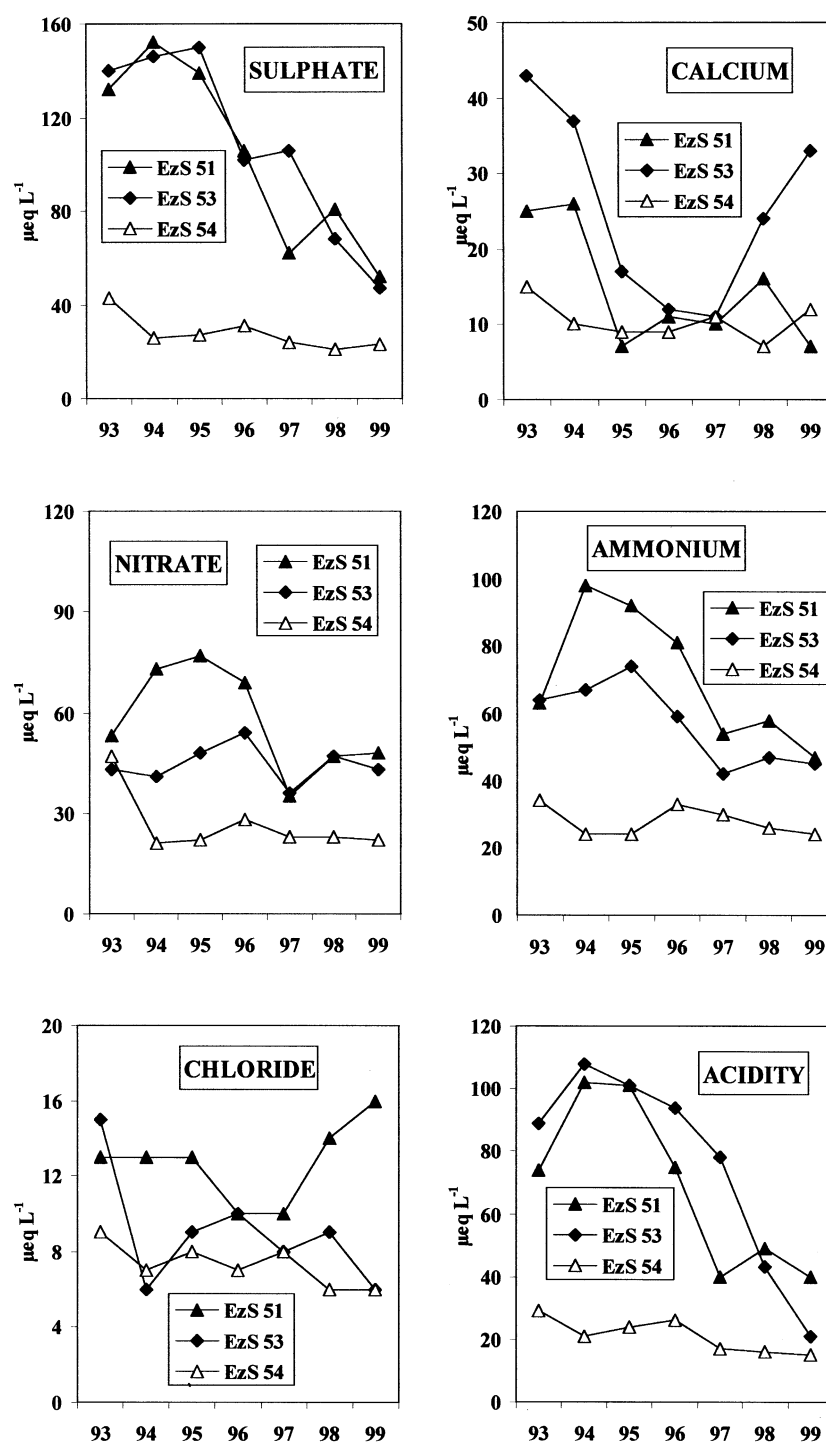


Fig. 7. Annual average volume-weighted concentration of sulphate, nitrate, chloride, calcium, ammonium, and the acidity in precipitation in Carlsfeld for EzS 51 (East Germany), 53 (Czech), and 54 (West Germany).

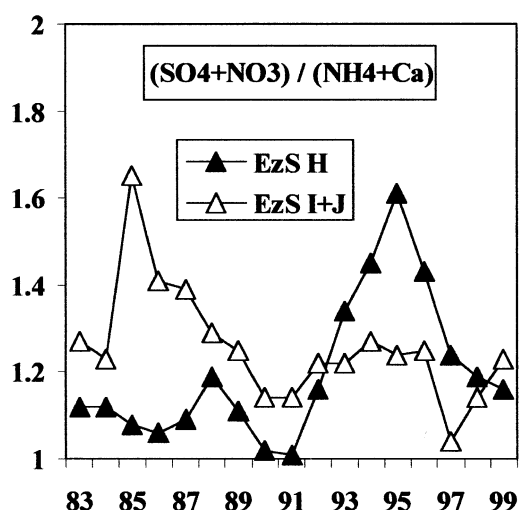


Fig. 8. Annual variation of concentration ratio (sulphate + nitrate)/(ammonium + calcium) in rain water for EzS H and I + J in Seehausen (concentration in $\mu\text{eq L}^{-1}$).

of sulphur- and CaO-rich lignite, as can be seen especially from the Seehausen data.

3.2.3. 1996–1999. The previous time period ended with the highest acidity. How would the trend develop in the ensuing years? The OMKAS project monitored the development of acidification and atmospheric pollutants in the Black Triangle during 1996–1999. It was possible to continue the measurements at the Carlsfeld site (beginning in 1993) and at the oldest operating site, Seehausen.

Figs. 5 and 7 show the annual volume-weighted mean concentrations of main components in precipitation in Seehausen and Carlsfeld. In Fig. 7 the polluted precipitation originating from the Czech Republic (EzS 53) can be identified. In Tables 1 and 2 all measured components of the main entry sectors H, I + J, and 51, 53, and 54 are listed separately. In the years after 1995 the sulphate content decreased from about 150 to 100 $\mu\text{eq L}^{-1}$ from 1995 to 1996 and up to 50 $\mu\text{eq L}^{-1}$ until 1999 for East Germany (EzS H and 51) as a result of desulphurization of power and heating plants. A second strong decrease in sulphate in precipitation from the Czech Republic (EzS 53) followed from 1997 to 1998 and 1999, by more than 50%, due to the closure and desulphurization of power and heating plants. In 1999

the sulphate concentration in precipitation from East Germany (EzS H and 51) and the Czech Republic (EzS 53) amounted to about 50 $\mu\text{eq L}^{-1}$, which was still twice that in rain water from West Germany sectors (EzS I + J and 54). The nitrate concentration in rain (between 40 and 50 $\mu\text{eq L}^{-1}$) from the Czech sector (EzS 53) remained stable. For the East Germany sectors (EzS H and 51) nitrate had a maximum in 1995 and then in 1997 returned its former value, remaining stable for the rest of the period (about 70 $\mu\text{eq L}^{-1}$ for EzS H and 50 $\mu\text{eq L}^{-1}$ for EzS 51), cf. Figs. 5, 7 and Section 3.2.2. The decrease in calcium concentration was completed in the third period. The calcium level for rain water of sector 51 (Carlsfeld) is now nearly the same as in rain from entry sectors in West Germany, but the rain of other sectors (EzS H and 53) still has higher values. The ammonium content in precipitation showed large variations. In general, a slightly downward trend dominates. The concentrations from West Germany sectors are always smaller than from East Germany and the Czech Republic.

From 1995 to 1996 the acidity in rain decreased remarkably from 120 to 60 $\mu\text{eq L}^{-1}$ and 100 to 75 $\mu\text{eq L}^{-1}$. In the period until 1999 a further decrease down to 30 and 40 $\mu\text{eq L}^{-1}$ in Seehausen (EzS East Germany H) and Carlsfeld (EzS East Germany 51) took place, respectively. In the precipitation from EzS 53 (Czech Republic) the acidity dropped from 80 to 20 $\mu\text{eq L}^{-1}$ in only two years (from 1997 to 1999 subsequent to a second strong reduction in the emission of pollutants (cf. Fig. 4). Some concentrations in precipitation are now lower compared to East Germany.

Nevertheless, as a consequence of the emission reduction in West Germany required by environmental regulations the concentration of components in rain also decreased by about 50% (for sulphate and acidity). Therefore, in 1999 the acidity in precipitation from East Germany and the Czech Republic (EzS 51, 53 and H) was still higher by 10–20 $\mu\text{eq L}^{-1}$ than in rain from West Germany sectors (EzS 54 and I + J).

Interannual changes in concentration due to differences in meteorological conditions may also play a role.

3.3. Meteorological influences

The direct emission–deposition relation is obviously influenced by meteorological conditions

Table 2. Annual average volume-weighted concentration for all measured components in $\mu\text{eq L}^{-1}$ for the EzS 51 (East Germany), 53 (Czech), and 54 (West Germany) in Carlsfeld

EzS	Year	<i>n</i>	H ⁺	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	NH ₄ ⁺	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺
51	1993	14	74	13	132	53	63	10	3	25	4
	1994	9	102	13	152	73	98	11	4	26	2
	1995	39	101	13	139	77	92	8	6	7	3
	1996	24	75	10	106	69	81	7	3	11	3
	1997	35	40	10	62	35	54	7	3	10	3
	1998	18	49	14	81	47	58	13	2	16	5
	1999	41	40	16	52	48	47	17	1	7	5
53	1993	12	89	15	140	43	64	9	6	43	8
	1994	12	108	6	146	41	67	4	5	37	2
	1995	13	101	9	150	48	74	5	3	17	4
	1996	19	94	10	102	54	59	7	3	12	3
	1997	19	78	8	106	36	42	4	2	11	3
	1998	22	43	9	68	47	47	8	2	24	8
	1999	13	21	6	47	43	45	6	3	33	10
54	1993	90	29	9	43	47	34	7	3	15	3
	1994	116	21	7	26	21	24	6	2	10	3
	1995	99	24	8	27	22	24	5	2	9	3
	1996	75	26	7	31	28	33	5	2	9	4
	1997	89	17	8	24	23	30	7	2	11	4
	1998	120	16	6	21	23	26	6	1	7	3
	1999	79	15	6	23	22	24	6	1	12	4

(Topol, 1986; Singh et al, 1987; Durana et al., 1992; Minoura and Iwasaka, 1997). The following influences can play a role:

- the wind speed in cloud level height over emission regions,
- the duration of precipitation/dry periods before the start of sampling,
- the type of precipitation (drizzle, rain, shower, or snow),
- fog during precipitation (only in mountains) and
- strongly convective events (mostly in the summer months and in mountains only).

Wind speed at cloud level, corresponding to the residence time of air masses above an emission region, influences the concentration of components in precipitation. Fig. 9 shows this effect for the example of annual mean concentration of components in rain water at the Seehausen site (EzS H, East Germany). In the former years the pollution of precipitation (e.g. sulphate and acidity) was higher at situations of lower wind speed at cloud level ($<250 \text{ km d}^{-1}$) in comparison to that of higher wind speed at cloud level

($>250 \text{ km d}^{-1}$). In recent years the differences have become smaller and have reached zero because pollution over East Germany strongly decreased.

The factors precipitation duration and time without rain before the onset of precipitation sampling are very important. The rain water components decrease with increasing duration of precipitation in the sequence $\text{H}^+ < \text{Cl}^- < \text{SO}_4^{2-} \sim \text{NO}_3^- < \text{NH}_4^+ < \text{Ca}^{2+}$ and can fall to less than 50% of the initial value after, e.g., a 12 h rain period during which the pH value, expressed as $[\text{H}^+]$, is practically constant. Dry periods before sampling have an inverse effect. The concentration in the first fraction increases by nearly the same amount after a dry period of two days (cf. Marquardt and Ihle, 1988).

Marquardt and Ihle (1988) also discussed the effect of the type of precipitation. Small droplets and rainout from lower heights cause a different quantity of substances in precipitation by drizzle than by rain and shower. From 1983 to 1989 the drizzle from the sectors of East Germany was more alkaline than in other kinds of precipitation. After 1993 this fact was reversed: the acidity in

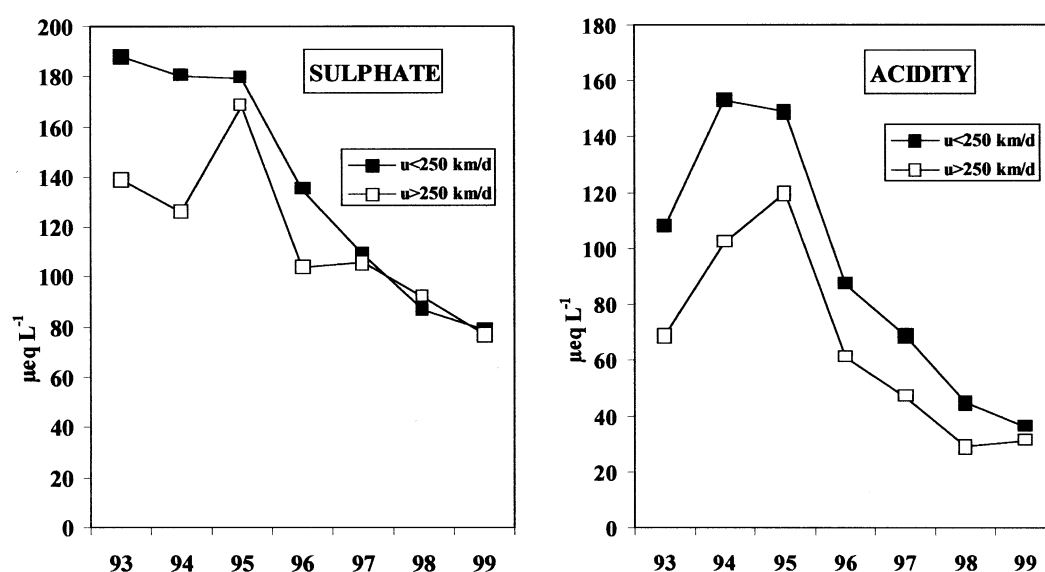


Fig. 9. Influence of wind speed of air masses ($u < 250 \text{ km d}^{-1}$ and $u > 250 \text{ km d}^{-1}$) at the concentration of components in rain water for EzS H in Seehausen from 1993 to 1999.

drizzle was higher than in rain (cf. Table 3). The strongly decreased dust emission (alkaline component) caused this change.

In situations of fog during precipitation (only at the mountain site Carlsfeld) in comparison with precipitation without fog the average content of sulphate and nitrate in rain water increased by approximately 20%, but the calcium concentration decreased by approximately 50%. As a consequence, the acidity content increased by approximately 40%.

4. Wet deposition

The wet deposition is the product of ion concentration ($\mu\text{eq L}^{-1}$) and amount of precipitation

(1 m^{-2} or mm) over the sampling time. The input of pollutants by wet deposition is strongly dependent on meteorological parameters (type, frequency, and duration of precipitation, wind direction etc., cf. Section 3.3) and amount of precipitation. The amount of precipitation can vary considerably from year to year in the different sectors, which is also true for the total sum. Table 4 contains the annual total amount of precipitation and the parts of sectors. Fig. 10 shows the percentage of amount of precipitation from the annual total amount of sites Seehausen and Carlsfeld for the measurement period.

In Seehausen the annual total amount of rain varied between 410 and 685 mm, which corresponds to 74–125% of the long-term average value of 550 mm. The values for Carlsfeld were found

Table 3. Sectoral mean acidity in $\mu\text{eq L}^{-1}$ in drizzle and precipitation for the EzS East Germany (H and 51), Czech (53), and West Germany (I+J and 54) in different time periods

Time period	Rain type	EzS 51	EzS 53	EzS H	EzS 54	EzS I+J
1983–1989	Drizzle			19		41
	Rain			45		31
1993–1996	Drizzle	142	137	113	29	29
	Rain	88	93	74	26	28
1997–1999	Drizzle	80	67	41	22	10
	Rain	40	54	35	16	9

Table 4. Total and sectoral precipitation amount (RR) in mm for Seehausen and Carlsfeld

Year	Seehausen			Carlsfeld			
	RR (mm) total	RR (mm) H	RR (mm) I + J	RR (mm) total	RR (mm) EzS 51	RR (mm) EzS53	RR (mm) EzS 54
1983	548	66	201				
1984	565	83	160				
1985	482	63	113				
1986	578	67	162				
1987	604	71	134				
1988	492	80	174				
1989	410	103	159				
1990	595	41	240				
1991	426	20	213				
1992	575	37	264				
1993	708	181	330				
1994	698	70	335	1294	43	117	555
1995	474	25	126	1517	181	48	517
1996	455	31	129	1020	109	57	324
1997	472	54	204	1115	95	82	331
1998	686	74	263	1446	55	77	547
1999	540	61	284	1173	149	43	417

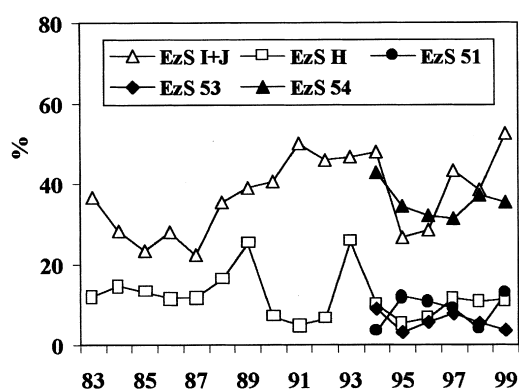


Fig. 10. The percentage of the amount of precipitation from the annual total amount for EzS East Germany (H and 51), Czech (53), and West Germany (I + J and 54).

to be between 1020 and 1510 mm, i.e. 82–123% of the long-term average of 1238 mm. For the interesting entry sectors differences in the annual amount of rain between 20 and 180 mm (EzS H), 45 and 180 mm (EzS 51), and 45 and 115 mm (EzS 53) were observed. These data correspond to fractions of 5–25%, 4–13%, and 3–7%, respectively, related to the total annual amount. On the other hand the amount of precipitation from the rain-rich sectors EzS I + J and EzS 54 was between 60 and 260 mm and 325 and 555 mm, respectively,

corresponding to between 22 and 52% and 32 and 43% of the total annual amount. These examples show that substantially smaller amounts of precipitation (only up to one eighth of the total annual amount of precipitation) came from the highly polluted areas of eastern regions, and the variation in the amount of rain was great.

In Figs. 11 and 12 the total wet deposition from sulphate sulphur, total nitrogen (sum of nitrate nitrogen and ammonium nitrogen), and acidity are presented for the sites Seehausen and Carlsfeld, for the entry sectors from West Germany (EzS I + J and 54), and eastern regions (EzS H and 51, 53).

The input of sulphate sulphur remained constant to 1988, showed a strong decrease in the total fluxes up to 1990/1991 and then a slight decline to 1999. This was caused from the decrease of SO₂ emission in the eastern industrial regions. The total nitrogen input remains constant with variations caused by different amounts of precipitation. The maximum input of acidity for EzS I + J in 1992–1994 results from the large contribution of the amount of the precipitation (cf. Table 4) and for EzS H in 1993 to 1994 additionally from the high concentration of acidity (cf. Table 1).

The precipitation from West Germany (EzS I + J and 54), with a precipitation fraction

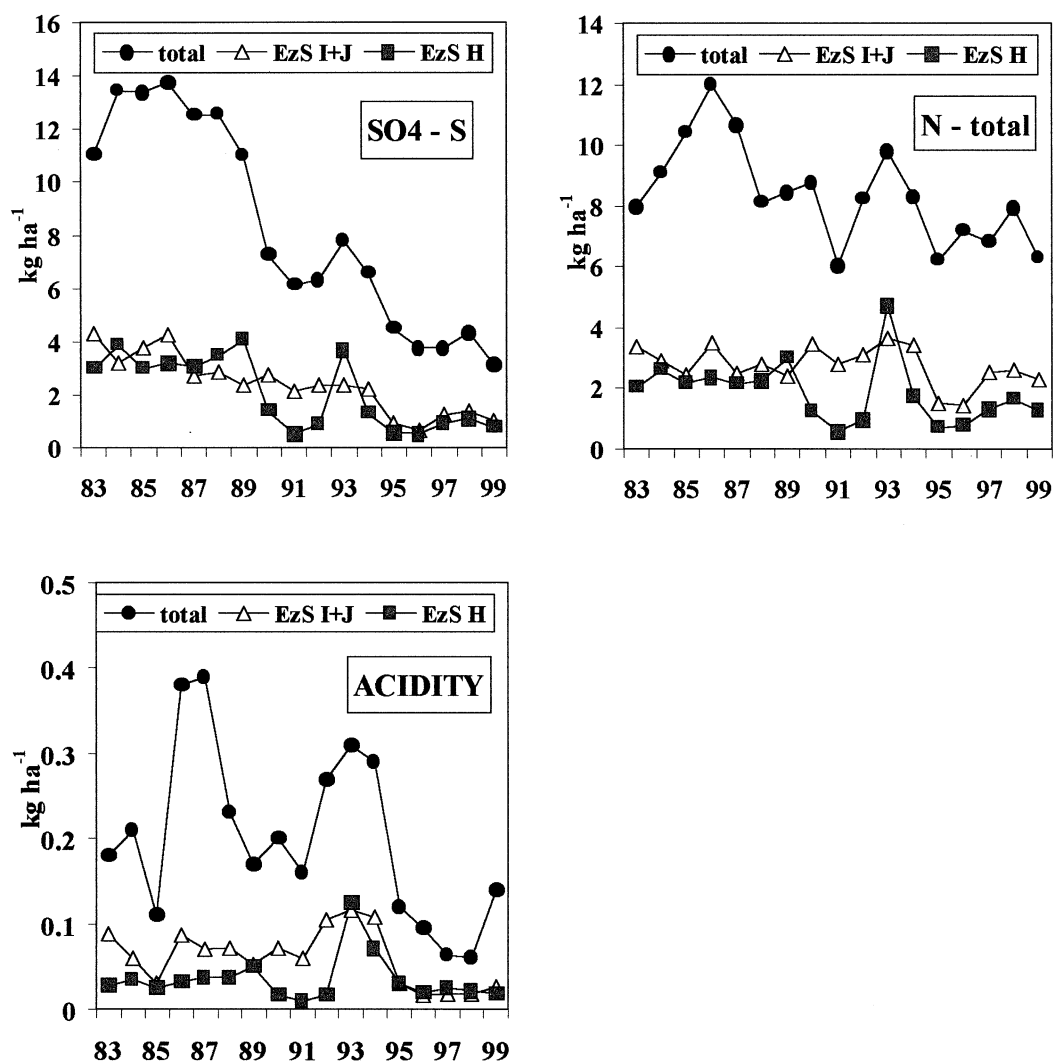


Fig. 11. Wet deposition for sulphate sulphur, total nitrogen (sum of nitrate nitrogen and ammonium nitrogen), and acidity in Seehausen for EzS H (East Germany), I + J (West Germany), and the annual total amounts.

maximum of about 30–50%, did not always show the expected largest contribution to the deposition. The amount of precipitation from sectors of western regions (I + J, 54) was, on average, up to ten times higher, but the deposition of components can also be only equal or partly lower than from eastern sectors (H, 51, 53), in which the concentration of components was higher (cf. Figs. 11 and 12).

5. Summary

The pollution of rain water is connected with a strong dependence of emissions of crossed areas incorporated in air masses and on meteorological parameters. With the help of short-term collection of rain water and the classification of the origin of raining clouds by entry sectors and back trajectories it could clearly be shown that changes

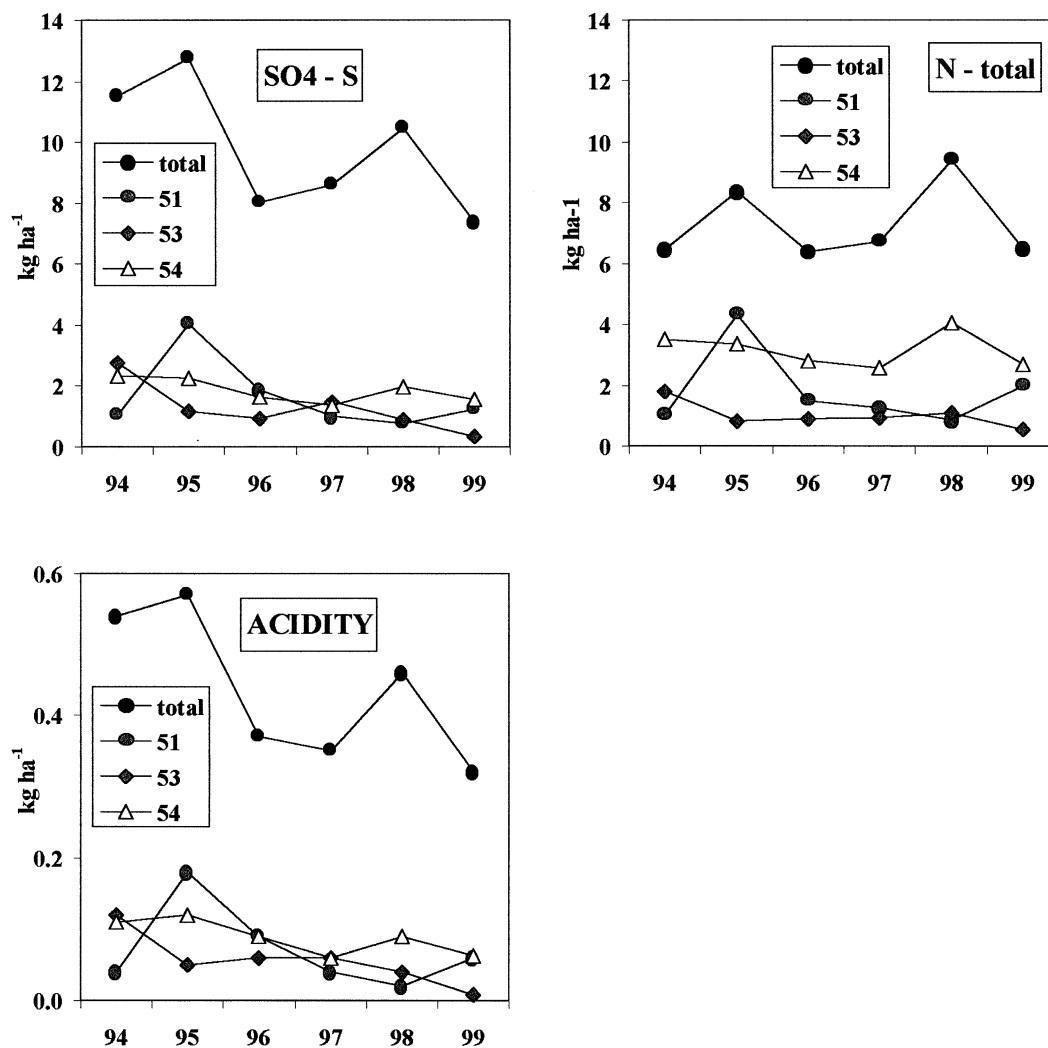


Fig. 12. Wet deposition for sulphate sulphur, total nitrogen (sum of nitrate nitrogen and ammonium nitrogen), and the acidity in Carlsfeld for EzS 51 (East Germany), 53 (Czech), 54 (West Germany), and the annual total amounts.

in emissions cause changes of components in precipitation.

The entry sectors have been characterized by similar emissions and/or geographical regions. In autumn 1982 investigations began at the Seehausen site. The examinations at this site were made without substantial changes in measurement technique up to 1999. Therefore this data set is the longest sector-classified measurement period, which is very important for trend statements.

The total investigation period can be subdivided

into three time periods. The period (from 1983 to 1989/90) is the time before the unification of Germany and was marked by large emissions of SO_2 (no desulphurization of flue gases), NO_x (obsolete industrial techniques), and dust (insufficient dust removal in flue gases). At the Seehausen site the average annual mean concentrations in this period were larger for sulphate ($275 \mu\text{eq L}^{-1}$) by a factor of two, for nitrate ($70 \mu\text{eq L}^{-1}$) by about two, for ammonium ($150 \mu\text{eq L}^{-1}$) by about two, for calcium ($158 \mu\text{eq L}^{-1}$) by about three, and,

finally, acidity ($45 \mu\text{eq L}^{-1}$) was equal for the entry sector East Germany compared to West Germany. The high emissions of acidifying components (SO_2 and NO_x) were compensated by alkaline components (Ca and NH_3), so that the acidity in rain water was about equal to those from the sectors under the influence of West Germany.

In the second period (1991–1995) the reformation and modernization of industry and agriculture lead to different effects on the emissions and consequently on the components in precipitation. Alkaline components were reduced efficiently by dust removal: calcium decreased by two thirds and ammonium by one third. The acidic sulphate component decreased by one half and nitrate increased by 40%. As a consequence, the acidity of rain water strongly rose, up to five times that in rain from West Germany.

The third period (1996–1999) is influenced by the effects of reformation of industry in the other eastern regions and was studied in the Black Triangle (South Saxonia, North Bohemia, and Silesia). In this phase desulphurization in the power plants of East Germany was established. The same took place in North Bohemia nearly two years later. Therefore, the rain water concentration of components decreased once more, at the Carlsfeld site more than in Seehausen, and the acidity had about nearly the same value in 1999 as in the first period. The ionic components in precipitation from East Germany and the Czech Republic (EzS H, 51, and 53) are still more abundant than in rain from West Germany (EzS I + J and 54), but now the contents are at a much lower level compared to before. For the coming

years it remains to be seen if the pollution of rain water from the eastern regions will decrease further.

Meteorological influences (wind speed, precipitation type, and duration) were included in the investigations. They can essentially affect concentrations (decrease and/or increase) of components in precipitation. Also differences in the concentration of components between flat and mountainous sites were found.

The impact of precipitation of the ecologically relevant components sulphur, nitrogen, and acidity were determined and compared for different sectors. The high variation of the amount of precipitation plays an important role. The fractions of rain water from the stronger polluted eastern regions (East and South) are essentially lower (in average four times) than from the cleaner western regions (Southwest to Northwest) and amounted to 5–20% of the total annual amount of precipitation, but the deposition of components by rain water was equal or higher than with rain water from western sectors until in the mid-1990s.

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REFERENCES

- Acker, K., Möller, D., Marquardt, W., Brüggemann, E., Wieprecht, W., Auel, R. and Kalaß, D. 1998. Atmospheric research program for studying changing emission patterns after german unification. *Atmos. Environ.* **32**, 3435–3443.
- Asman, W. A. H. and Jaarsveld, H. A. 1992. A variable-resolution transport model applied for NH_x in Europe. *Atmos. Environ.* **26**, 445–464.
- Brüggemann, E., Gnauk, Th. and Renner, E. 1995. Bestimmung von Spurenstoffen in Niederschlagsproben. *Umweltwissenschaften und Schadstoff-Forschung, Zeitschrift für Umweltchemie und Ökotoxikologie* **5**, 261–264.
- Brüggemann, E. and Rolle, W. 1998. Changes of some components of precipitation in East Germany after the unification. *Water, Air, and Soil Pollution* **107**, 1–23.
- Brüggemann, E. and Spindler G. 1999. Wet and dry deposition of sulphur at the site Melpitz in East Germany. *Water, Air, and Soil Pollution* **109**, 81–99.
- Buijsman, E., Maas, J. F. M. and Asman W. A. H. 1987. Anthropogenic NH_3 emissions in Europe. *Atmos. Environ.* **21**, 1009–1021.
- Casado, H., Encinas, D. and Lacaux, J. P. 1992. The moderating effect of the Ca^{2+} ion on the acidity in precipitation. *Atmos. Environ.* **26**, 1175.
- Durana, N., Casado, H., Ezcurra, A., Garcia, C., Lacaux,

- J. P., Pham Van Dinh 1992. Experimental study of the scavenging process by means of a sequential precipitation collector – Preliminary result. *Atmos. Environ.* **26**, 2437–2443.
- Federal Government to the Deutscher Bundestag 1997. *Sixth Air Quality Report* of the Federal Government. Ed.: Federal Ministry of Environment, Nature, Protection, and Security, Box 120629, D-53048 Bonn, Germany.
- Friedrich, W. 1968. Aschekatalog des Institutes für Energetik, Leipzig.
- Friedrich, R., Wickert, B. and Laing, R. K. 1996. Bestimmung und Modellierung der Emission umweltrelevanter Schadstoffe. In: *SANA – Final Report A 1.2*.
- Gantz, H. 1993. Erstellung eines Emissionskatasters für Verkehr. In: *SANA-Annual Report A 1.4*.
- Gnauk, Th. and Rolle, W. 1998. A three-year study of nonmethane hydrocarbons in surface air over Saxony (Germany). *J. Atmos. Chem.* **30**, 371–395.
- Huntzicker, J. J., Cary, R. A. and Ling, C. S. 1980. Neutralization of sulphuric acid by ammonia. *Environ. Sci. Technol.* **14**, 819–824.
- Likens, G. E. 1989. Acid rain and its effects on sediments in lakes and streams. *Hydrobiologia*, 331–348.
- Marquardt, W., Ihle, P. and Kappe, W. 1986. Automatischer großflächiger Niederschlagssammler für Spurenstoffanalysen. *Chem. Tech.* **38**, 262–263.
- Marquardt, W. and Ihle, P. 1988. Acidic and alkaline precipitation components in the mesoscale range under the aspect of meteorological factors and the emission. *Atmos. Environ.* **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**, 665–670.
- Marquardt, W. and Brüggemann, E. 2000. Nationale und grenzüberschreitende Auswirkungen von Emissionen auf Niederschlagskomponenten in sächsischen Grenzregionen. In: *Final report of project OMKAS*, 32–37, Ed.: Sächsisches Landesamt für Umwelt und Geologie, Zur Wetterwarte 11, D-01109 Dresden, Germany.
- Marquardt, W., Brüggemann, E. and Heintzenberg, J. 1996a. Cleaning Eastern Germany with an acid bath. *AMBIO* **25**, 215–216.
- Marquardt, W., Brüggemann, E. and Ihle, P. 1996b. Trends in the composition of wet deposition: effects of the atmospheric rehabilitation in East Germany. *Tellus* **48B**, 361–371.
- Minoura, H. and Iwasaka, Y. 1997. Ion concentration changes observed in drizzling rains. *Atmos. Res.* **45**, 165–182.
- Möller, D., Acker, K., Marquardt, W. and Brüggemann, E. 1996. Precipitation and cloud chemistry in the Neue Bundesländer of Germany in the background of changing emissions. *Időjárás* **100**, 117–133.
- Munger, J. W. and Eisenreich, S. J. 1983. Continental-scale variations in precipitation chemistry. *Environ. Sci. and Technol.* **17**, 32A–42A.
- Okochi, H., Kameda, H., Hasegawa, Sh., Saito, N., Kubota, K. and Igawa, M. 2000. Deterioration of concrete structures by acid deposition – an assessment of the role of rainwater on deterioration by laboratory and field exposure experiments using mortar specimens. *Atmos. Environ.* **34**, 2937–2945.
- Olendrzynski, K. 2000. Performance of EMEP Eulerian Acid Deposition Model for 1998. EMEP/MSC-W 2000, ISSN 0332–9879.
- Reimer, E. and Scherer, B. 1992. An operational meteorological diagnostic system for regional air pollution and long term modelling. In: *Air Pollution Modelling and its Application* (eds.: H. van Dop and G. Kallos), NATO Challenges of Modern Society, **17**, Plenum Press, New York, London, 565–572.
- Schulz, M. and Friedrich, W. 1967. Differential-thermoanalytische und thermographimetrische Untersuchungen an Braunkohleaschen. In: *IfE-Report 2/1689/67 F*, Institute of Energetics (IfE), Leipzig.
- Singh, B., Nobert, M. and Zwack, P. 1987. Rainfall acidity as related to meteorological parameters in Northern Quebec. *Atmos. Environ.* **4**, 825–842.
- Sutton, M. A., Dragosits, U., Tang, Y. S. and Fowler, D. 1999. Ammonia emissions from non-agricultural sources in the UK. *Atmos. Environ.* **34**, 855–869.
- Topol, L. E. 1986. Differential in ionic compositions and behaviour in winter rain and snow. *Atmos. Environ.* **2**, 347–355.
- Zimmermann, F. and Bothmer, D. 2000. Die Emissionssituation im Schwarzen Dreieck, gestern-heute-morgen. In: *Final report of project OMKAS*, 15–22, Ed.: Sächsisches Landesamt für Umwelt und Geologie, Zur Wetterwarte 11, D-01109 Dresden, Germany.