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TROPOSPHÄRENFORSCHUNG

# Long-time trends of acidification in rain water at the outskirts of Leipzig and the rural site Melpitz (Germany)

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## INTRODUCTION

Changes in concentration of pollutants in rain water caused by changes in emissions were investigated at the outskirts of Leipzig and the rural site Melpitz in East Germany beginning in 1992. The emission situation in East Germany was characterised by high amounts of  $\text{SO}_2$ ,  $\text{NO}_x$ ,  $\text{NH}_3$ , and dust due to combustion of low-quality lignite with high sulphur and/or salt and ash contents (Figure 1). After the German reunification in 1990 the emission fluxes of  $\text{SO}_2$ ,  $\text{NO}_x$ ,  $\text{NH}_3$ , and dust changed substantially in a short time. First, the collapse of industry and agriculture reduced the emission of all pollutants. Then, the waste gas cleaning was improved strongly, but the flue gas desulphurisation technique was only partly established. As a consequence, the basic components of emissions were reduced more than the acidic ones. Therefore, the mean  $\text{H}^+$  concentration in rain water amounted  $40.6 \mu\text{eq l}^{-1}$  (pH value = 4.39) in the period 1992 to 1996. In the middle of 1996 the flue gas desulphurisation technique has been mandatory for all power and heating plants. The  $\text{SO}_2$  emission could be reduced considerably again and the mean  $\text{H}^+$  concentration decreased to about  $19.7 \mu\text{eq l}^{-1}$  (pH value = 4.71) in the period 1997 to 2004 (see below).

## EXPERIMENTAL

The rain water investigations were begun in the German project SANA (Scientific Programme for recovery of the atmosphere; from 1992 to 1995) and continued up to now. The urban measurement site Leipzig lies at the north-easterly outskirts of Leipzig ( $12^\circ 23' \text{E}$ ,  $51^\circ 20' \text{N}$ , 113 m asl) and the rural site Melpitz west of the city Torgau (12 km) and northeast of the Halle-Leipzig area (41 km,  $12^\circ 54' \text{E}$ ,  $51^\circ 32' \text{N}$ , 86 m asl), see Fig. 2. The main wind direction is westerly and to a lesser degree south-easterly. Precipitation samples were collected usually 24hr by automatic wet-only sampler at 1.5 m above ground. The data capture rate for rain events was about 85%. In precipitation eight main components ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ) were analysed by ion chromatography (Metrohm) as well as acidity (pH value), conductivity, and meteorological parameters.

Data quality was assessed by an ion balance and conductivity check for each sample. Further, quality control was given through participation in interational ring analysis by WMO-EPA each year. A detailed description is given e.g. by:  
- Brüggemann et al., 1995  
- UWSF-Umweltchemie Ökotoxik. 7, 261-264  
- Brüggemann and Rolle, 1998  
- Water, Air, and Soil Pollution 107, 1-23  
- Brüggemann and Spindler, 1999  
- Water, Air and Soil Pollution 109, 81-99  
- Marquardt et al., 2001  
- Tellus 53B, 529-545

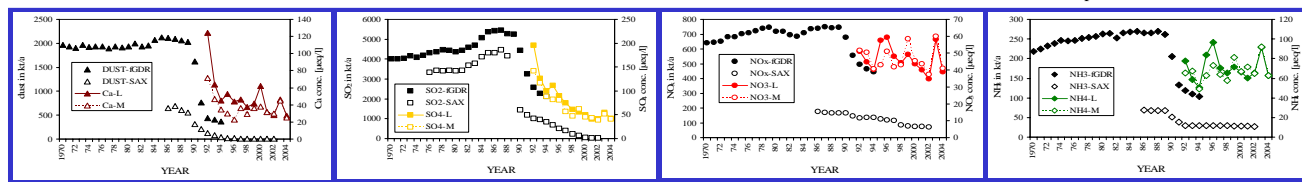


Fig. 1: Annual variation of emissions in former GDR (GDR) and Saxony (SAX) as well as annual average volume-weighted concentration of precipitation components at sites Leipzig (L) and Melpitz (M)  
(Sources for emission data: Federal Government to the Deutscher Bundestag (1997) Sixth Air quality Report of the Federal Government. Ed.: Federal Ministry of Environment, Nature Protection, and Security, Box 120629, D-53048 Bonn;  
Emission land-register of Saxony: <http://www.umwelt.sachsen.de/fur>; Zimmermann and Bothmer (2000) Die Emissionssituation im Schwarzen Dreieck, gestern-heute-morgen. Final Report of project OMKAS, Ed.: Sächsisches Landesamt für Umwelt und Geologie, Zur Wetterwarte 11, D-01109 Dresden, Germany)

## RESULTS

The acidic content of precipitation is usually dependent on the presence of acids ( $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ , and organic acids). The neutralisation of these compounds occurs in the presence of basic components (ammonium and calcium). The pH value of precipitation follows from the ratio between these acids and bases.

In Figure 4 the trend of acidity in rain water is shown at sites Leipzig and Melpitz. An increase of extreme acidity values in precipitation was observed at both sites in the summer months up to 1996. The maximum acidity was  $468 \mu\text{eq l}^{-1}$  (pH value = 3.33) at site Leipzig in 1996. The mean summer  $\text{H}^+$  concentration amounted to about  $50 \mu\text{eq l}^{-1}$  (pH value = 4.3) in the time period 1992 to 1996 and  $20 \mu\text{eq l}^{-1}$  (pH value = 4.7) in the period 1997 to 2004. The changes of pH value distribution are shown in Figure 5. It can be seen that the relative frequency (RF) of samples with pH values below 4.0 amounted between 5 and 10% up to 1996 and then, the pH below 4.0 was found only rarely. The RF of samples with pH values between 4.0 and 4.5 decreased from about 50% in 1992 (sites L and M) to about 20% at site L and 30% at site M in 1997 and remained roughly constant up to 2004. For pH values between 4.5 and 5.0 the RF of samples remained stable between about 30-40% at site Leipzig as well as 30-50% at site Melpitz. The RF of samples with pH values above 5.0 varied in the time period of 1992 to 1996 between about 15-30% at site L and 5-20% at site M. Since 1997 up to 2004 the RF amounted about 40-50% (site L) and 30-40% (site M). The mean annual pH value increased from about 4.35 in 1992 to 4.8 in 2004 (Figure 6).

The changes of acidity of precipitation were mainly influenced by the changes of main ionic components as sulphate, nitrate, calcium, and ammonium. Sea-salt had only a marginal influence at these sites.

Figure 3 presents the trend of the main components in rain water between 1992 and 2004. In 1992 sulphate and calcium were predominant by prevailing lignite burning in power and heating plants in the regions Halle/Leipzig and Lausitz as well as by domestic heating in this urban region. In 2004 ammonium had the highest concentration in rain water followed of sulphate and/or nitrate and calcium with the smallest concentration. The nitrate and ammonium concentration in precipitation remained roughly stable, whereas the  $\text{NO}_x$  and ammonia emissions were reduced by shut-down of older industrial and agricultural facilities. The drastic increased traffic (the number of vehicles grew by the factor of 1.5 from 1989 to 1995) appears to have compensated these reductions. The Ca decrease in rain water was finalised in 1993/1994 by the application of efficient dust removal techniques in power and heating stations and use of alternative fuels. The sulphate decrease in precipitation was caused by the drastic reduction of  $\text{SO}_2$  emissions (closure of power and heating plants, decreased amount of used lignite, substitution of lignite by other sources of energy) up to 1995. Since summer 1996 the flue gas desulphurisation technique has been mandatory for all power and heating plants.

The temporal different reduction of acidic (mainly sulphate) and basic (mainly calcium) rain water components can be seen also in the ratios of the ionic components (Figure 7). The sulphate/calcium ratio increased from 1992 to 1996 from 1.7 to 2.4 (mean annual data) and then it decreased to about 1.5 up to 2004. The sulphate/nitrate ratio was very high in 1992 (mean annual data for Leipzig was about 4 and for Melpitz about 3). This ratio dropped and since 1998 it varies around 1. In 2003 the ratio was below 1 at first. The  $(\text{Ca}+\text{NH}_4)/(\text{SO}_4+\text{NO}_3)$  ratio (mean annual data) at site Leipzig amounted to about 0.8 and in Melpitz to about 0.7 in 1992. Since 1996 the ratio increased and amounted about 1 in 1997. Since 2000 it varies around 1.2 up to 2004. This means that the acidic components in rain water overbalanced the basic components up to 1996.

The wet deposition is the product of ion concentration ( $\mu\text{eq l}^{-1}$ ) and amount of precipitation ( $\text{L m}^{-2}$  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.), concentration of components, and amount of precipitation. The amount of precipitation can vary considerably from year to year. In Figure 8 the total wet deposition from nitrate-nitrogen, ammonium-nitrogen, sulphate-sulphur, and acidity as well as the precipitation volume are presented. The nitrate- and ammonium-nitrogen remains roughly constant with variations caused by different amounts of precipitation. The mean annual deposition of ammonium-nitrogen (mean annual data at site Leipzig: 5.7 kg/ha and Melpitz: 4.8 kg/ha) is mostly higher as the nitrate-nitrogen (mean annual data at site Leipzig: 3.8 kg/ha and Melpitz: 3.3 kg/ha). The input of sulphate-sulphur showed a strong decrease up to 1996 (mean annual data in Leipzig: from 18 to 7 kg/ha, Melpitz: from 10 to 5 kg/ha), then a slight decline to 1999, and remained roughly constant (mean annual data in Leipzig: about 4.0 kg/ha, Melpitz: about 3.6 kg/ha) to 2004. The calcium input decreased to 1996 (mean annual data in Leipzig: from about 14 to 4 kg/ha, Melpitz: from about 6.6 to 3 kg/ha) and then varied at these values up to 2004. The input of acidity amounted about 3 kg/ha up to 1996 and decreased to about 1 kg/ha in 1997 and varied at this value to 2004.

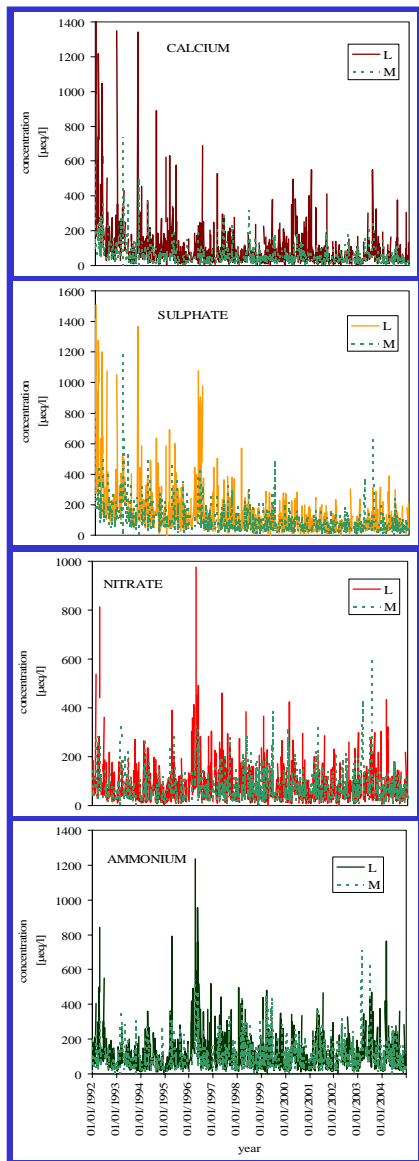


Fig. 3: Trends of daily component concentrations in rain water at sites Leipzig (L) and Melpitz (M)

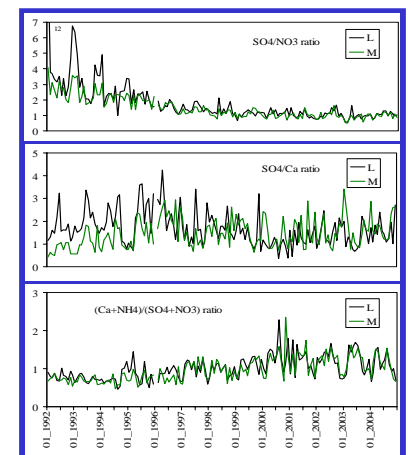


Fig. 7: Trend of component ratio (monthly data) at sites Leipzig (L) and Melpitz (M)

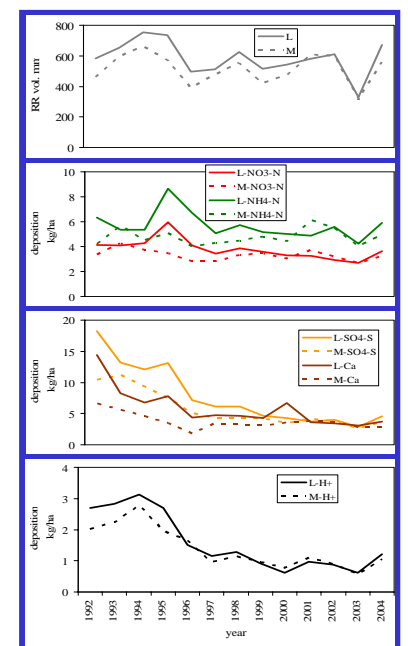


Fig. 8: Precipitation volume variation and trend of component deposition (monthly data) at sites Leipzig (L) and Melpitz (M)

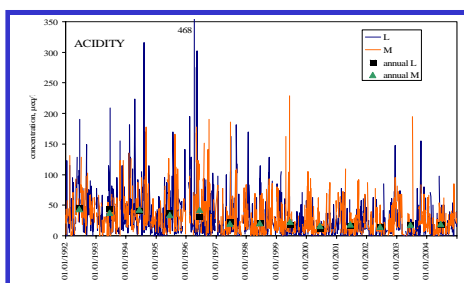


Fig. 4: Trend of acidity (daily values – lines, annual volume-weighted values – points) in rain water at sites Leipzig (L) and Melpitz (M)

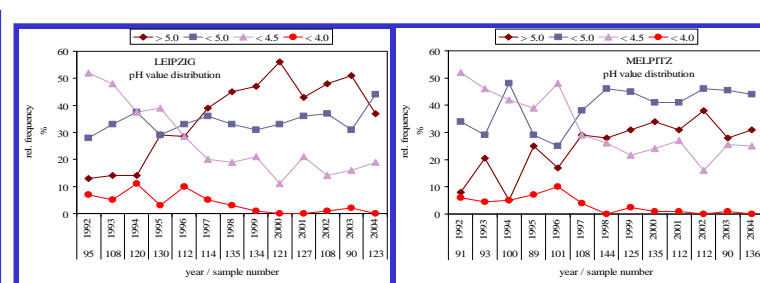


Fig. 5: Annual pH value frequency distribution at sites Leipzig and Melpitz

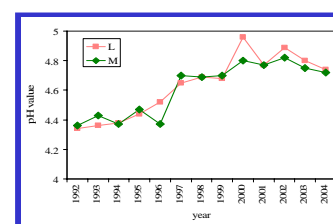


Fig. 6: Mean annual pH values at the sites Leipzig (L) and Melpitz (M)

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