tion, the causes of the decline of forests in central Europe are discussed. The influence of acidification in modifying the terrestrial and aquatic vegetation and in decreasing the number of the species is treated in detail by Roelofs. This author, as does Schuurkes, attaches great importance to the oxidation of ammonium in acidifying the soil and affirms that, at least in the Netherlands, the major damage to the vegetation is due to the ammonium and sulphur compounds and not to ozone. The effects of acidification on soil and water microorganism, macrophytes, aquatic invertebrates, phyto- and zooplankton and amphibians are described in the papers by Francis, Grahn, Økland, Geelen and Leuven. Each of these papers reports fully on the most recent information on the group considered and gives a clever criticism of the results. In addition, up-to-date references, tables and figures enrich these papers; for example, the paper by Økland includes 159 references and 20 illustrations. The biological indicators of acidification are described and discussed by Johnsen. This author reports some examples of the use of mosses and lichens in detecting and mapping the level of air polluted by sulphur oxides. The acidification experiments in natural (lakes and streams) and artificial (outdoor channels and 'enclosures') aquatic ecosystems is the subject of the paper by Ravera. The author compares the results obtained with these methods with those obtained from investigation using water bodies acidified by atmospheric depositions. The most important advantages of acidification experiments are the following: the early effects (which have never been recorded in natural ecosystems acidified by depositions) may be observed; the pre-acidification is known as well as the intensity, rate and duration of the acidification; the effects due to the hydrogen ion concentration may be isolated from those of other pollutants. The paper by Kramer is the last in the list of the contributions, because, in my opinion, it represents the conclusion of this review. Indeed, it concerns the past, the present and the future trends of ecosystem acidification. The author, after having discussed the present and past knowledge of acid deposition, illustrates some important statements on future emission of sulphur oxides. He underlines the large potential variability in predicting the sulphur emissions for the near future, because several factors interacting with each other may influence the predictions: for example, the rate and quality of industrial development and the changes of the amount and types of fuel used in relation to the different sensitivity of the ecosystems.

The distribution of acid deposition in Germany

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Summary. The distribution of acid deposition by atmospheric precipitation in the Federal Republic of Germany is discussed, based on investigations of the wet H^+-deposition during the five years 1980–1984, using a network of 16 automated samplers of our own construction located in various categories of ecosystems. Analytical problems of sampling and the electrometric determination of pH in rainwater are briefly discussed. Results for the average amounts of precipitation, the average H^+-concentrations and average H^+-depositions in the 16 typical regions of the Federal Republic of Germany are compared and the influences of meteorological parameters are discussed. An increase of the H^+-concentration and H^+-deposition values has been observed from 1980 onwards with a maximum in 1981 and a slow decrease in the next two years. The comparison of the values found for rural regions with those for more significantly polluted regions shows that in the latter regions the removal of H^+-ions by wash-out is more effective. Whereas in the Ruhr region the pH is shifted to more acid values, due to the wash-out of acid particles and aerosols, in regions with metallurgical industry the pH is shifted to more alkaline values due to the wash-out of alkaline particles. In general the free acid in rain and snow is rather uniformly distributed over the whole area as a result of mesoscalic transport of the acid precursors SO_2 and NO_x and the concomitant formation of acid in the cloud droplets leading to acid deposition by rain-out. The composition of rainwater and the possibility of determining the proportion of the acid anions in rain which are of anthropogenic origin is briefly discussed.

Key words. Acid rain; rainwater; sampling network; acid distribution; acid deposition; wet deposition; pH; precipitation amount; hydrogen ion concentration.

1. Introduction

Acidification of precipitation due to anthropogenic input has been recognized as one of the most severe environmental problems. The chemical composition of a raindrop is the integral result of the incorporation of aerosol particles as well as the absorption of trace gases. Both processes are effective from the beginning of heterogeneous nucleation of water molecules which form a cloud element, and continue until the raindrop reaches the ground.

Absorption of gaseous trace substances takes place both within the clouds as below the clouds. One result of this interaction between trace substances and droplets in the air is acidification of rainwater. If only carbon dioxide (concentration ca. 330 ppmv) were present as a trace substance besides water molecules, for rainwater a pH value of about 5.6 would be the result. In general, however, lower values are found. This additional acidity is due to the incorporation of acidic substances, predominantly sulphuric or nitric acid, by the droplets.

Sulphuric and nitric acid are atmospheric contaminants resulting to a large extent from oxidation of sulphur and nitrogen oxides, SO_2 and NO_x emitted from stationary and (for NO_x) also mobile combustion sources. The oxidation takes place as a homogeneous reaction in the gas phase and in the cloud droplets or a heterogeneous reaction at the surface of dry aerosol particles or those loaded with a water film. The predominant reaction path in the homogeneous phase is the reaction of sulphur and nitrogen oxides with OH radicals formed photochemically in the atmosphere[1,29].

Conversion of SO_2 to H_2SO_4 in a polluted atmosphere occurs by homogeneous oxidation with strong oxidizing radicals such as OH, HO_2, CH_3O_2[4,8]. The source of these radicals are hydrocarbon and NO_x emissions, which produce oxidizing radicals as intermediate products by photo-oxidation during daytime. The conversion of NO_x to HNO_3 takes place in a series of complicated reactions during which nitrogen oxides undergo various oxidation stages and eventually end up as HNO_3[27,28].

In the case of SO_2 small condensation nuclei are formed directly, due to a negligible saturation vapor pressure of the sulphuric acid. These cloud-active nuclei grow by condensation and coalescence into cloud and rain droplets. In the case of NO_x the formation of such cloud-active nuclei is improbable, as the saturation vapor pressure of the nitric acid is relatively large. The oxidation of the gases SO_2 and NO_x dissolved in the cloud droplets is catalyzed by some heavy metal ions (Fe, Mn, V) and oxidation agents (H_2O_2, O_3). In aerosol particles sulphuric and nitric acids are formed in an analogous manner by heterogeneous catalytic oxidation and reaction with water[30]. The reaction rates of these oxidation processes and consequently their contribution to the formation of sulphuric and nitric acid depend strongly on local conditions, especially on the concentration of aerosol particles.

Annual emissions in t/a of SO_2 and NO_x in the Federal Republic of Germany (FRG) are summarized in tables 1 and 2 according to the most important emission sources. 90% of the SO_2 emission originates from fossil fuel burning power plants and from industry, especially heavy industry; i.e. from well-defined point and area sources. This type of emission can be drastically reduced by the introduction of new combustion techniques. About one half of the SO_2 emission is exported from the FRG to neighboring countries. On the other hand, due to the prevailing wind direction, about the same amount of SO_2 is imported into the FRG from the neighboring countries situated in the prevailing SW wind direction. The most important emittent of NO_x is the automobile traffic with 45% of the total. A further 50% stems from fossil fuel burning power plants and industry. The currently discussed introduction of a catalyzer for the elimination of NO_x from automobile exhausts will reduce the NO_x emission by about 80%, which corresponds to a reduction of the total NO_x emission by about one third[10,13,34].

The deposition of acid with precipitation depends among other influences on meteorological parameters which change distinctly from year to year. Therefore, to gain insight into the trends of the deposition of acid and its seasonal variations the measurements have to be performed over years and the dependence on meteorological parameters should be taken into account. Moreover, all typical ecosystems of the country have to be incorporated in the sampling network to obtain relevant deposition data.

Another problem to be solved is the sampling and the pH measurement of the rainwater sample. The hitherto-used open samplers for the total (wet and dry) deposition (e.g. the Bergerhoff sampler[19]) do not guarantee the true measurement of pH as the acid and/or alkaline components of the dust sampled during the dry period change the original pH value of the rainwater sample.

A systematic two years' study of the deposition of acid and other pollutants in the FRG was undertaken by Georgii[6], Gravenhorst[9] and Perseke[26] in 1979–1981. A sampling network consisting of 10 stations located in various ecosystems and equipped with a combined wet and dry sampler of their own construction was installed. In 1980 a systematic long term investigation on the deposition of acid and ecotoxic heavy metals by rain and snow was launched by our institute, and it is still being continued[21]. A network of 19 automated wet-only precipitation samplers of our own construction has been distributed over the country. Among the sampling stations those of Georgii's network are also included. The comparative evaluation of the data for the period 1980–1984, presented in this paper, reveals the main contours of the deposition situation for free acid in the FRG and extends, modifies and deepens conclusions based on data previously available for 1980–1982 only[12,22–24]. The evaluation of the wet deposition of acid is based on the accurate electrometric determination of H^+-concentration in rain and molten snow.

2. Methodological aspects

The main problems in getting reliable data on the concentration of acid in rain and the deposition of acid with precipitates are the collection of appropriate samples,

Table 1. Annual SO_2-emission in the FRG

Emittent group	SO_2 in 10^6 t/a	%	S-equivalent in 10^6 t/a
Fossil fuel fired power plants	2.06	59.4	1.03
Industry	1.02	29.5	0.51
Household	0.31	9.0	0.16
Traffic	0.08	2.1	0.04
Total emission	3.47	100	1.74

Table 2. Annual NO_x-emission in the FRG

Emittent group	NO_x in 10^6 t/a	%
Fossil fuel fired power plants	0.94	31.3
Industry	0.58	19.3
Household	0.14	4.7
Automobile traffic	1.34	44.7
Total emission	3.0	100

their stability and the accurate pH determination in a medium with a low conductivity.

2.1 Sampling

To avoid a contamination of the rainwater sample by dust particles during dry periods, wet-only sampling is the only reliable procedure. This can be achieved in principle manually if a suitable sampling vessel is exposed at the beginning of a rainfall and taken away immediately after the end of the rainfall. However, for large-scale field measurements the only useful device is an automated rainwater sampler. Severe criteria for the design, the installation and the operation of the automated rainwater sampler have to be fulfilled to ensure its perfect performance[15]. The most important of them are the following: the necessity to collect all of the rain from the very beginning of the rainfall, exclusion of contamination of the rainwater sample by the material of the sampler and by contact with the polluted atmosphere, and the prevention of changes in the composition of the sample by biological processes and by evaporation.

Taking into account these criteria and automated sampler has been developed (fig. 1)[16]. Controlled by a humidity sensor it opens only during the precipitation periods, excluding thus any interference by dustfall during the dry periods. The humidity sensor is adjusted to open at the onset of drizzle rain but remains insensitive to fog. Electric heating, controlled by the ambient temperature ensures reliable operation down to −30 °C. Rain water (or molten snow) flow through the polyethylene funnel into a filtration device. Suspended matter that can influence the pH of the sample during the sampling period is filtered off with a membrane filter of 0.45 µm pore size. The filtrate is collected in a polyethylene flask. All polyethylene components that come into contact with the sample have been subjected before use to special cleaning procedures[14]. The top of the sampler is situated about 2 m above ground, excluding thus interference by the splashing of soil particles during heavy rainfall. An automated sampler of Erni[17] is designed in a similar way. Both wet-only samplers are often applied in the FRG and are commercially available[2,3].

2.2 Measurements of H^+-concentration and of major ions

The free acidity for rain is expressed by the activity of hydrogen ions present. In the case of rain the activity of H^+ can be approximated by the H^+-concentration. It is commonly expressed in terms of pH scale where pH is defined as the negative logarithm of the H^+-concentration. The H^+-concentration in rain is determined electrometrically using a glass electrode specially designed for low coducting media, e.g. the Ross combination electrode with 3 M KCl, with which pH can be determined down to 8 µS/cm. The electrode has to be calibrated frequently with two NBS buffers of pH 4.0 and 7.0. The precision of the pH measurement should have an accuracy of at least 0.03 pH-units. Accuracy should be established by interlaboratory calibration. The rainwater samples have to be stored in polyethylene vessels in the dark and at about −20 °C to avoid biological activity. The samples should be analyzed within 2 weeks after sampling. More details on pH measurement in rainwater and molten snow are given elsewhere[20].

The anions SO_4^{2-}, NO_3^- and Cl^- present in rainwater or molten snow as the main anionic components can be most satisfactorily determined by fully automated ion

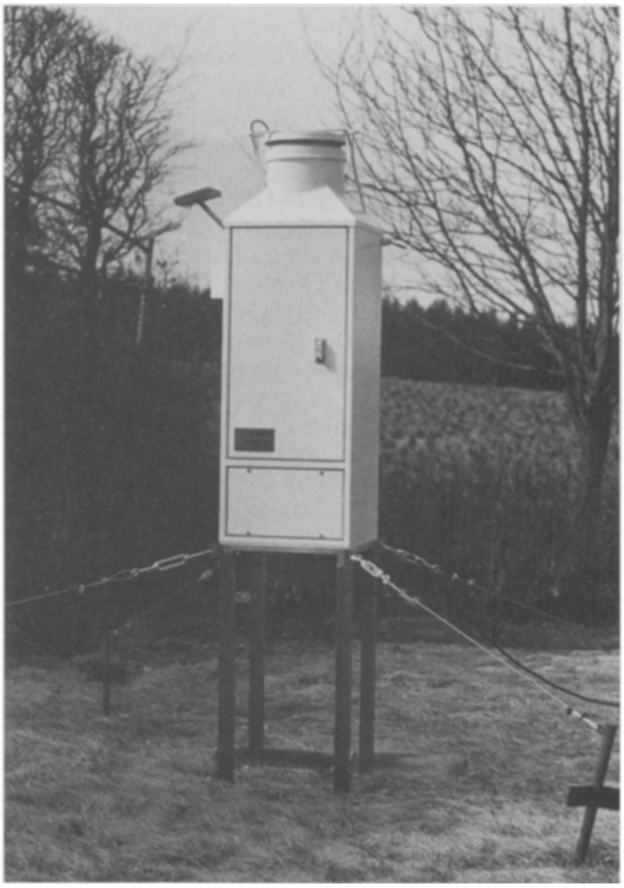

Figure 1. Automated precipitation sampler at field station.

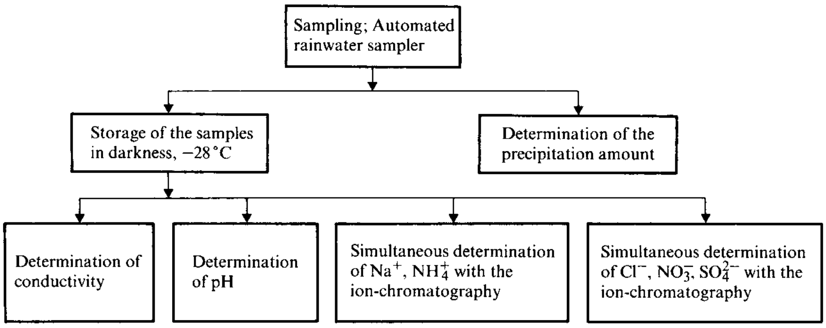

Figure 2. Flow chart of analytical procedure.

chromatography. The samples should be stored in polyethylene vessels in darkness at −28 °C and analyzed within a week after collection. The application of ion chromatography to the determination of the major anions and cations in rainwater is described elsewhere[32]. The total analytical procedure is summarized in the flowchart in figure 2.

3. Results and discussion

3.1 Sampling network

The sampling network of the institute consists of 34 automated rainwater samplers distributed over different ecosystems of the FRG and some neighboring countries. Some of the samplers were not in operation over the whole period 1980–1984. Here the results for a selected group of 16 typical sampling stations (underlined in the following list) are given. The stations are located in four different kinds of region (fig. 3):

a) rural regions without strong point or area emission sources and having only a basic low pollution burden: List/Sylt, Schleswig, Winsen, Bückeburg, Frenz, Inden, Jülich, Grebenau, Witzenhausen, Deuselbach, Kleiner Feldberg, Königstein, Hof, Schauinsland, Hohenpeissenberg, Berchtesgaden, Arbon (Switzerland), Horgen (Switzerland), Yerseke (Netherlands), Emma Haven (Netherlands), b) polluted urban areas: Hamburg-Poppenbüttel, Hamburg-Billbrook, Braunschweig, Frankfurt, Saarbrücken, München, c) heavily polluted Ruhr region: Essen, Dortmund, d) polluted regions with metallurgical industry: Goslar, Stolberg-Binsfeldhammer, Stolberg-Werth, Stolberg-Gressenich, Stolberg-Münsterbusch, Stolberg-Kohlbusch.

Most of these stations are situated at the respective station of the 'Deutscher Wetterdienst' (German Meteorological Service), two of them (Deuselbach, Schauinsland) at the stations of the UBA (Federal Environmental Protection Agency). Stations at Dortmund and Saarbrücken are operated in cooperation with university institutes. The respective meteorological data were supplied by these stations or the corresponding branches of German Meteorological Service.

3.2. Precipitation amount

The wet deposition of acid depends on both the actual H^+-concentration in rainwater and the precipitation amount. For the study of the changes of pH and the H^+-deposition during a single rain event the pH-measurement can be performed in short time intervals, e.g. 20 min, using a special sampler with an automated sample changer[9,20]. In this study, however, long term changes of pH and of the H^+-deposition have been investigated over five years and therefore a cumulative sampling on weekly basis has been performed. The average monthly precipi-

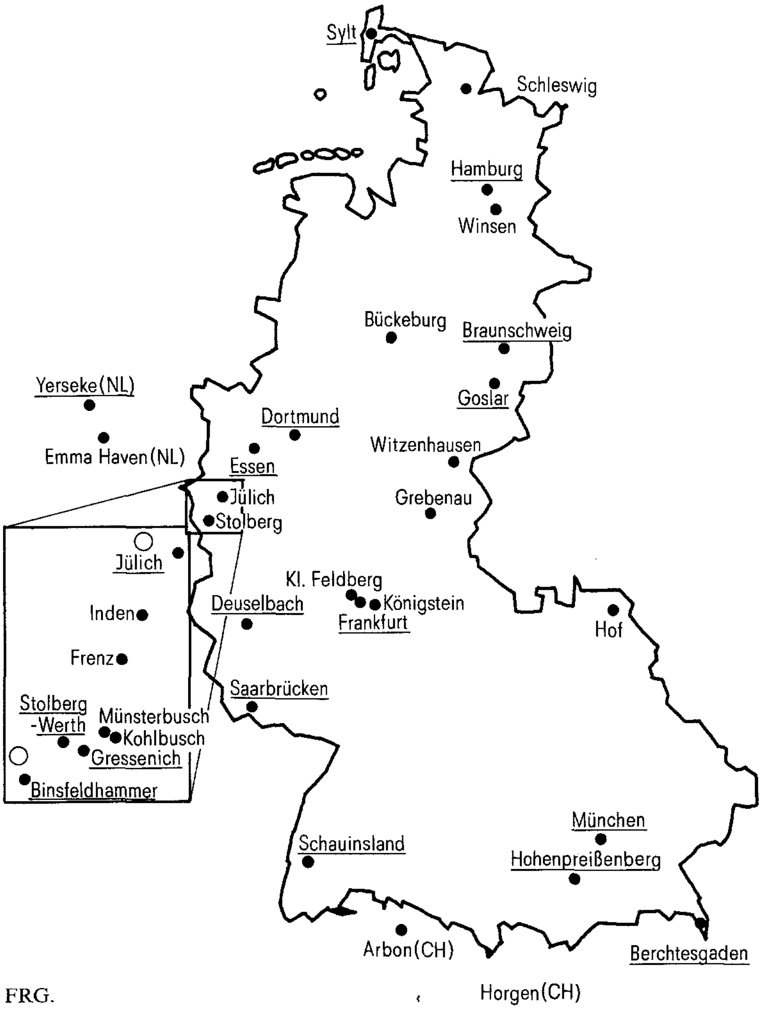

Figure 3. Sampling network in the FRG.

tation amounts were calculated from our data and compared with the data obtained with the official (national) raingauge by the Meteorological Service[18]. In general the data from both sources were in agreement within 15–20%.

The average daily precipitation amounts (yearly averages) in the years 1980 to 1984 for the chosen 16 stations in typical ecosystems of the FRG are presented in figures 4A, B and C. The data are expressed in l/m^2 and are numerically equal to data given in the official unit of mm. It can be seen from figure 4a that, with the exception of the hill stations at Schauinsland and Hohenpeissenberg, for the rural stations the average values of the precipitation amounts lie between 1.7 and 2.7 l/m^2. The higher values in the latter two stations (up to 5.7 l/m^{2}d) are caused by their elevated altitude (Hohenpeissenberg 988 m, Schauinsland 1284 m above sea level, resp.). The average deposition amounts are largest in 1981. At the stations of the other categories (figs 4b and c) the average deposition amounts lie between 1.6 and 3.6 l/m. The precipitation data will be correlated with the H$^+$-deposition data later.

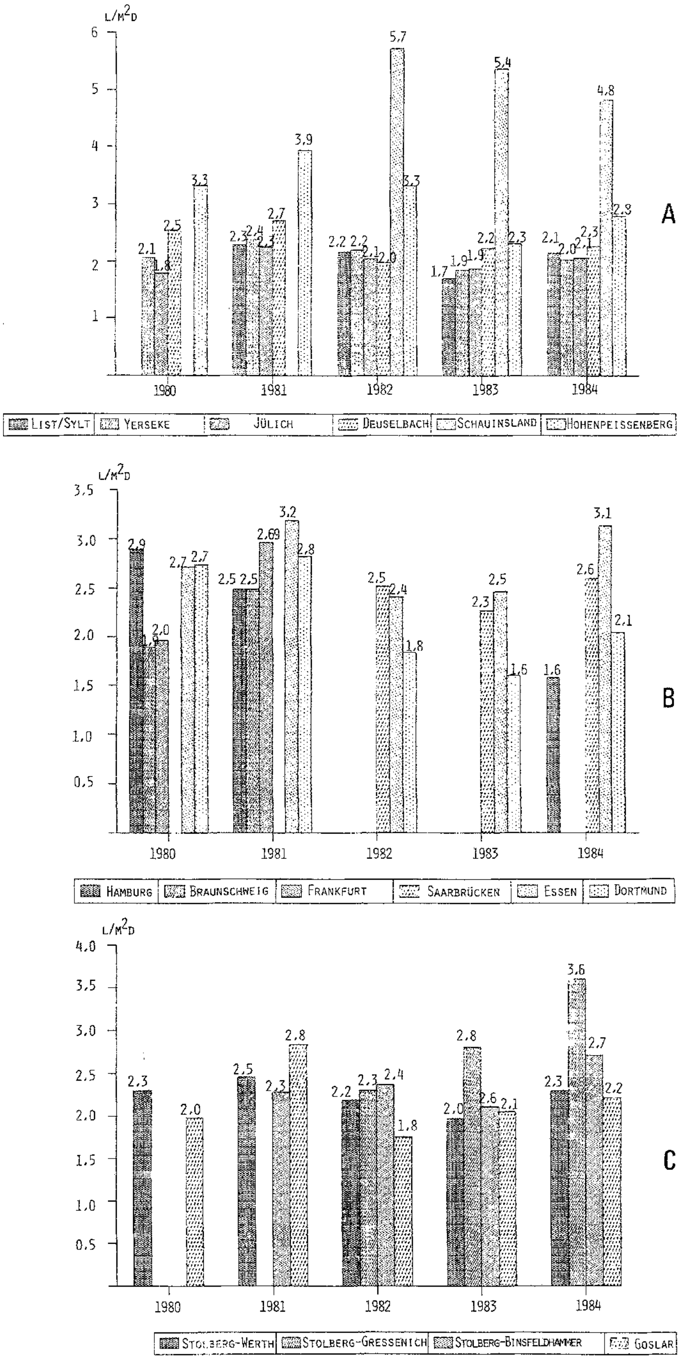

Figure 4. Average daily precipitation amount in *A* rural regions, *B* urban areas and the Ruhr region, *C* in regions with metallurgical industry. Sampling period 1980–1984.

In table 3 the precipitation data from 1980 to 1984 are summarized and compared with the average precipitation in Germany for the years 1931–1960. It can be seen, that, in 1981 the precipitation amount was exceptionally large; it is elevated in 1980 but only marginally elevated for 1982–1984. Thus, the last three years, and possibly also the year 1980, can be considered as average years from the viewpoint of the precipitation amount.

In table 3 the months of maximum and minimum precipitation amounts have also been stated and for comparison the average daily precipitation amount in rural stations is listed. The station Schauinsland was not installed before 1982 and therefore is not included. These data correlate well with the range of the yearly precipitation amount in the FRG, given also in table 3, and can thus be considered as a good estimate of the average daily precipitation amount in the FRG for the years considered.

It is known that the form of wet precipitation also plays a role in the deposition of acid. In table 4 the number of days with wet precipitation and the kind of wet precipitation in the FRG are summarized.

It can be seen that in a year precipitation occurs on more than half of the days. About one third of the days of a year have a precipitation amount > 1 l/m^2, and on less than one quarter snowfall occurs. In the year 1981 all of these data reached a maximum.

A windrose giving the average distribution of wind directions in Essen over 1980–1984 is shown in figure 7. The

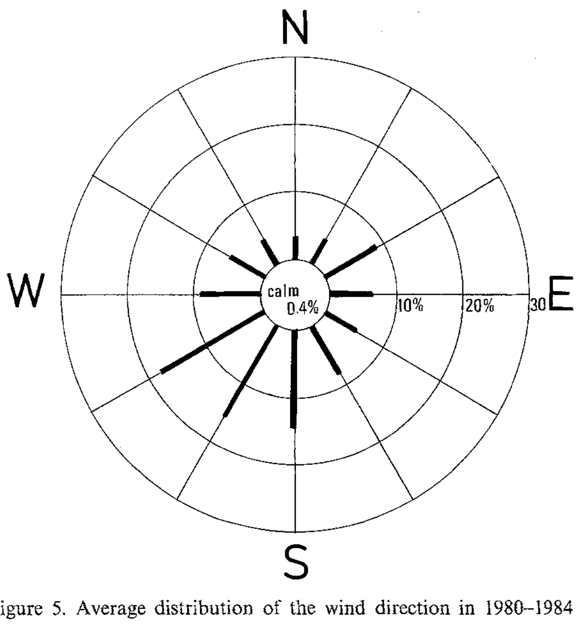

Figure 5. Average distribution of the wind direction in 1980–1984 in Essen.

Table 3. Precipitation amounts at the stations of the FRG sampling network in the years 1980–1984 and their relation to the average precipitation amount in 1931–1960

Year	1980	1981	1982	1983	1984
Annual precipitation amount (l/m^2)	650–1210	800–1450	640–1220	590–1140	620–1170
Deviation from the average 1931-1960 (%)	+ 3 to + 38	+ 13 to + 49	– 8 to + 18	– 8 to + 23	– 9 to + 27
Maximum precipitation amount	June, July	Oct., Dec.	Oct. Dec.	May	May, Sept.
Minimum precipitation amount	Febr., March	April	Febr.	Febr., July, Aug.	April, Aug.
Average daily precipitation amount (rural regions) (l/m^2d)	2.4	2.7	2.4	2.0	2.3

wind direction is preferentially from SWW to S with a maximum frequency at SWW. Nevertheless, the directions from W and NEE are also rather frequent. The wind direction at other stations was rather similar and it changed only marginally during 1980–1984.

3.3. *H^+-concentration in the wet precipitation*

The free acidity of rain is expressed by the concentration of hydrogen ions present. The H^+-concentration is also influenced by the concentrations of major anions and cations in the rain and snow, i.e. SO_4^{2-}, NO_3^-, Cl^-, HSO_4^-, HCO_3^-, NH_4^+, Na^+, K^+, Ca^{2+} and Mg^{2+}[7,11]. In the majority of cases the ions H^+, NH_4^+, SO_4^{2-} and NO_3^- are the most important ions determining the free acidity of rain. The importance of the ionic composition of rain will be treated in more detail later. Here the trends of the H^+-concentration in rain and snow at the 16 selected sampling stations during 1980–1984 will be discussed. The average monthly and yearly concentrations $\bar{c}$ are weighted means. They are calculated from the H^+-deposition according to equation (1).

$$\bar{c} = \frac{\Sigma d}{\Sigma p} = \frac{\Sigma c \cdot p}{\Sigma p} \qquad (1)$$

where c, p, and d are the H^+-concentration, the precipitation amount and the H^+-deposition, respectively, in a cumulative rainwater sample on a weekly basis. To calculate a mean value of the pH, the determined pH-values are transformed to H^+-concentrations. From the weighted average H^+-concentrations an average pH-value is obtained.

In figure 6A the average yearly H^+-ion concentrations are given for 6 rural stations. There are striking differences in the values between the station with the exception of the year 1980. The H^+-concentrations at stations located on hill crests (Schauinsland and Hohenpeissenberg) is distinctly lower than in other stations. These data, indicate that removal of H^+ from the atmosphere by wash-out and rain-out processes is somewhat dependent on the altitude and on other local parameters. Moreover, there is a tendency, observed also by other authors[25], for the H^+-concentrations to decrease with the precipitation amount. This effect smoothes the differences in the H^+-deposition in various regions, as described later.

At the other stations (figs 6B and 6C) the influence of the wet precipitation amount on the H^+-concentrations in rain is not so pronounced. Relatively high H^+-concentrations (up to 118 µg/l) were observed for stations situated in the heavily polluted Ruhr region, especially in Dortmund, in the years 1981–1983. The station in Essen is situated far away from the city center and therefore the values are in general not so high.

On the other hand the H^+-concentrations in regions with metallurgical industry, i.e. Stolberg and Goslar, exhibit rather low values which are comparable to those in rural regions. For the majority of stations an increase of H^+-concentrations from 1980 onwards can be noticed yielding a maximum value in 1982 followed by slow decrease in 1983 and 1984. This trend could be caused to some extent by the variation of SO_2 and NO_x emission during these recent years.

An additional insight into the trends of the H^+-concentrations in rain and snow is given by monthly pH variation in rural regions, polluted industrial regions and urban areas. In figures 7 and 8 the monthly averages of pH values during the years 1983 and 1984 are given with their ranges indicated by the standard deviations. In both years the monthly pH pattern in polluted regions (curves 2) is shifted to lower pH values compared with the pH pattern for rural regions (curves 1). Nevertheless, the course is rather similar, e.g. the minimum in June 1983 and the maximum in the winter months in 1983, the minimum in April 1984 and the maximum in the winter months in 1984.

This observation underlines the conclusion that the free acid in rain and snow is rather uniformly distributed over the whole area of the FRG and results mainly from a mesoscalic transport of NO_x and SO_2 and that the acid is formed preferentially during this transport in the cloud droplets (rain out). In general the pH is lower in winter than during other seasons which may be caused by the influence of humidity on the acid formation. No correlation with the precipitation amount can be observed. A yearly cycle of precipitation pH values was also studied by Georgii[6], Gravenhorst[9] and Winkler[33] but a noticeable

Table 4. Days with wet precipitation at the stations of the FRG sampling network during the years 1980–1984

Year	1980	1981	1982	1983	1984
Days with wet precipitation > 0.1 l/m^2	170–222	195–242	155–196	167–218	168–209
Days with wet precipitation > 1 l/m^2	110–160	131–169	99–142	114–152	116–140
Days with snow fall	24– 91	48–108	19– 68	20– 75	37– 87
Days with snow cover	16–138	40–136	2–125	20– 75	9–121

lowering of pH in polluted regions was not observed by these authors. This may be the result of differences in sampling technique, i.e. the separation of rainwater from dust particles by filtration in the rainwater sampler in our case.

It can be seen from figures 7 and 8 that the range of the monthly pH-values given by the standard deviation is in some cases rather large (up to more than one pH-unit) especially in polluted regions. This is caused not only by the differences between the stations in a particular category, but still more by the influence of dust particles and aerosols on the free acid level in rain. The dust particles can be basic and will accordingly increase the pH. In contrast some dust particles are acidic. The presence of such acid particles, or other aerosols, formed from the interaction with gaseous sulphuric or nitric acid, could lower the pH. These processes take place in the clouds, i.e. the incorporation of material into cloud droplets and still more during the wash-out which occurs when material below the cloud is swept out of the air by rain or snow as it falls. The wash-out processes are dominant close to the sources of pollution[1]. This is evidenced by the different yearly average H$^+$-concentrations values in polluted and rural regions given in figures 6A, B and C. It seems

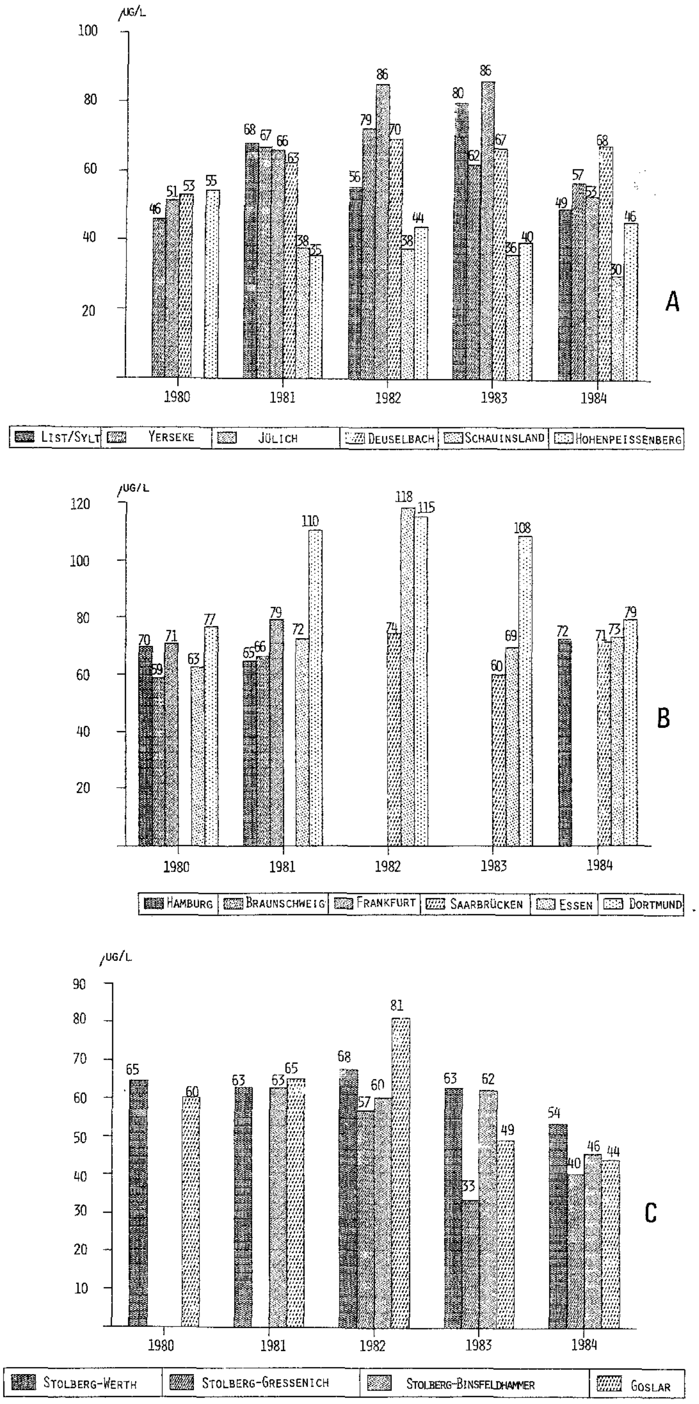

Figure 6. Average H$^+$-concentration (weighted yearly average) in *A* rural regions, *B* in urban areas and the Ruhr region, *C* in regions with metallurgical industry. Sampling period 1980–1984.

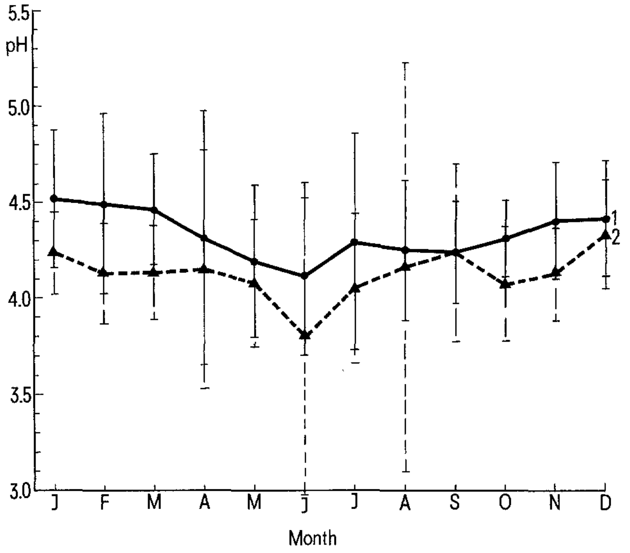

Figure 7. Monthly pattern of the pH of rain in 1983 in rural regions (Jülich, Yerseke, Sylt, Deuselbach, Schauinsland, Berchtesgaden, Hohenpeissenberg: curve 1) and in urban areas and the Ruhr region (Hamburg, Saarbrücken, München, Dortmund, Essen: curve 2).

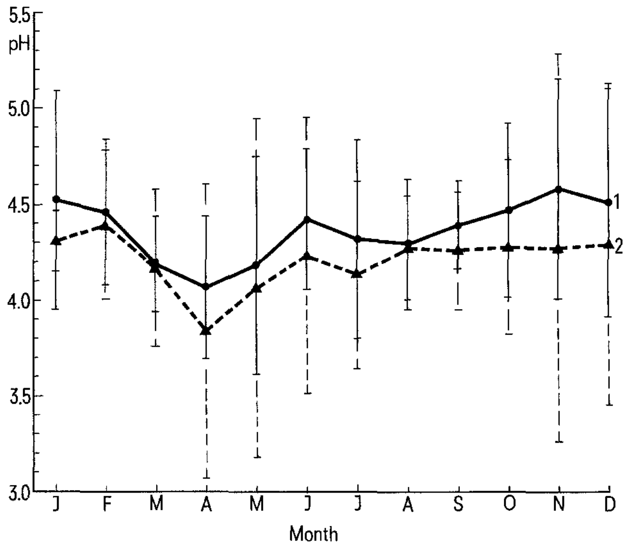

Figure 8. Monthly pattern of the pH of rain in 1984 in rural regions (Jülich, Yerseke, Sylt, Deuselbach, Schauinsland, Berchtesgaden, Hohenpeissenberg, curve 1) and in urban areas and the Ruhr region (Hamburg, Saarbrücken, München, Dortmund, Essen: curve 2).

that in the Ruhr region the influence of acid aerosols predominates whereas in regions with metallurgical industry basic dust particles prevail.

This conclusion is supported by the plots of the relative cumulative frequency of pH values in four typical stations from rural and polluted regions of the FRG given in figure 9. All curves start at the rather low pH of 3.3–3.6 but differ substantially in the 50% values and in the final values. The range of pH values lies between 1.4 for Dortmund and 3.8 for Hohenpeissenberg, which corresponds to a ratio of the largest to the lowest H^+-concentration of 25 for Dortmund and of 6000 for Hohenpeissenberg. The rather low 50% values lie at pH 4.0 in Dortmund, 4.2 in Deuselbach, 4.3 in Stolberg – with two frequency maxima at 4.0 and 4.3 – and 4.4 in Hohenpeissenberg. These results are in good agreement with earlier measurements of the relative cumulative frequencies in Frankfurt/M, Deuselbach and Hof in 1979–1980 by Perseke[26].

3.4 *H^+-deposition*

The H^+-concentrations in rain seldom reaches such elevated values that it could cause direct damage to vegetation. An exception is tree damage caused by direct interaction between a leaf or pine needle and acid rain or mist. More frequent is indirect damage caused by alteration of the root environment, i.e. the acidification of the soil.

This type of damages is not directly influenced by the actual H^+-concentration in rain but by its cumulative action, i.e. by the H^+-deposition with precipitation over a prolonged time period, Σt, e.g. a month or a year. The weighted mean of the H^+-deposition $\bar{d}$ in a period Σt is calculated from the H^+-concentrations c_t and the precipitation amount p_t in the respective sampling period t according to equation (2)

$$\bar{d} = \frac{\Sigma c_t\, p_t}{\Sigma t} \qquad (2)$$

For the amount of precipitation the values given by the Meteorological Service were used.

In figure 10A the average daily H^+-deposition at 6 rural stations are presented. It can be seen that the variations between the stations located on hills (Schauinsland, Hohenpeissenberg) with an elevated precipitation amount and other rural stations are not so pronounced as the variations of the H^+-concentrations (see fig. 6A).

This is caused by the smoothing effect of the large precipitation amount on the H^+-concentrations discussed above in part 3.3.

Therefore, the trend over the years 1980–1984 observed for H^+-concentrations, with a maximum in 1982, is less pronounced in the H^+-deposition. In general no correlation between the precipitation amount and the H^+-deposition can be detected. A steady decrease of the H^+-deposition from 1982 onwards – with the exception of Deuselbach – is still observable. This might be caused by some decrease in the emission of the acid precursors SO_2 and NO_x.

The average daily H^+-depositions in polluted urban areas and the Ruhr region are shown in figure 10B. The values are noticeably higher than at rural stations and also the range – from 110 to 309 $\mu g/m^2$ – is more expanded. Obviously, local effects of the wash-out of acid particles and aerosols are active in these regions, due to a higher emission of acid precursors. Here, a maximum of the H^+-deposition is reached in 1981 and after a decrease in 1982 and 1983 a new increase in 1984 occurs. These trends are partially caused by the changes in the precipitation amount as can be seen by comparing figure 10B with figure 4B.

The average daily H^+-depositions for the regions with metallurgical industry, represented by stations in the Stolberg region and at Goslar, are shown in figure 10c. The values are consistently lower than those in rural regions. This is obviously caused by the wash-out of basic particles which shift the pH to higher values. In some

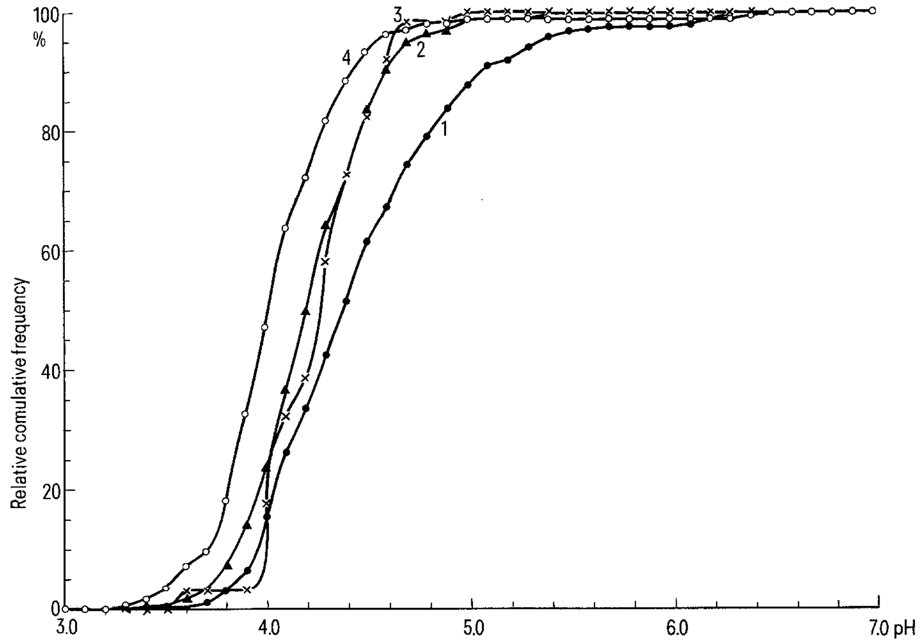

Figure 9. Relative cumulative frequency of the pH of rain in 4 ecosystems of the FRG: Hohenpeissenberg 1980–1984, 251 samples, pH range 3.44–7.22 (curve 1); Deuselbach 1980–1984, 412 samples, pH range 3.42–6.7; (curve 2); Stolberg 1983–1984, 215 samples, pH range 3.34–6.46 (curve 3); Dortmund 1983–1984, 121 samples, pH range 3.60–5.01 (curve 4).

cases, e.g. in the years 1980, 1981 and 1984, a correlation with the precipitation amount can be detected. A survey of the H^+-deposition data in the semidecade 1980–1984 in various regions of the FRG and some regions of Switzerland and the Netherlands in given in table 5. The differences between various region categories discussed above are clearly seen. The agreement with the data of Perseke et al.[26] in 1981 is good but in 1980 some severe discrepancies appear. As the sampling periods are not exactly the same the data are not strictly comparable. The values in De Bilt[6] in comparison with earlier values[31] are too low, perhaps due to the contamination of the sample by dustfall.

3.5 Composition of rainwater

The acidity of rain is almost exclusively determined by the concentrations of the major ions H^+, NH_4^+, SO_4^{2-} and NO_3^-. These ions are supplied by the strong inorganic acids H_2SO_4 and HNO_3, alkali sulphate and nitrate, and the weak inorganic base NH_4OH. As rainwater represents a diluted aqueous electrolyte solution these ions are completely independent of each other. Wet deposition of SO_4^{2-}, NO_3^- and Cl^- in various regions of the FRG was studied by Georgii[6], Gravenhorst[8] and Perseke[26] in 1979–1981. A comparative study of the anionic deposition of

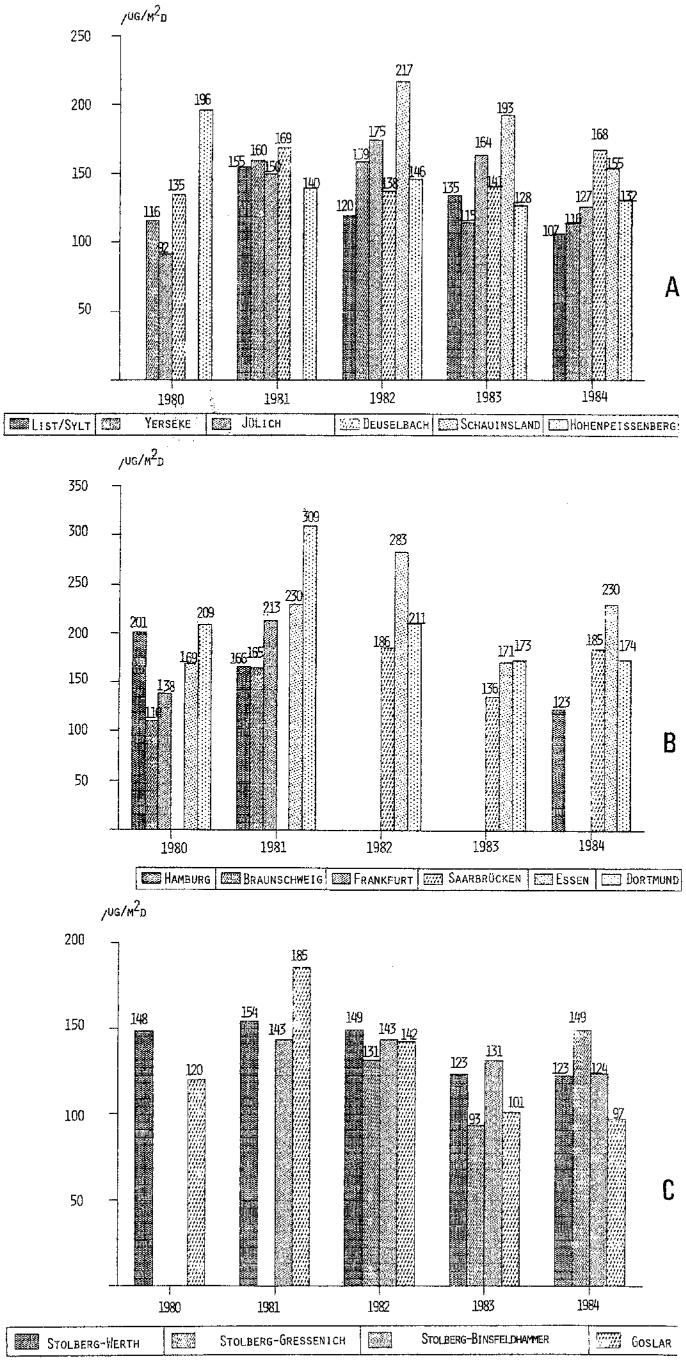

Figure 10. Average daily H^+-deposition (weighted yearly average) in *A* rural regions, *B* in urban areas and in the Ruhr region, *C* in regions with metallurgical industry. Sampling period 1980–1984.

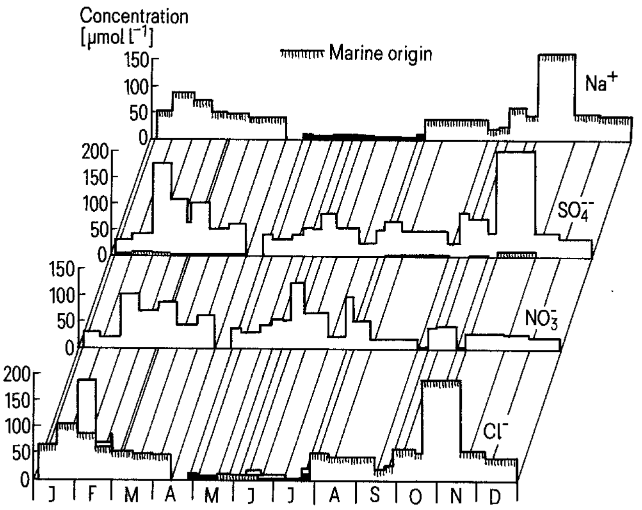

Figure 11. Concentration of the major cations and anions of rain at Stolberg in 1983.

Table 5. Average daily H^+-deposition in µg/m²d in various region categories of the FRG and in some regions of Switzerland and the Netherlands

Year	1980	1979/80[26]*	1981	1980/81[26]*	1982	1983	1984
Region category							
Rural region	90–160	60–140	150–170	105–150	120–175	115–160	110–170
Prealpine and alpine region	200	60	140	170	150–220	130–190	130–155
Urban areas	110–200	80–130	165–200	120–195	190	140	120–185
Ruhr region (Essen, Dortmund)	170–210	111	230–310	200	185–210	190–210	170–230
Regions with metallurg. industry (Goslar, Stolberg)	130–150	–	140–185	–	130–150	90–130	100–150
De Bilt, NL (rural)[5]**	95		91		60	–	–
Yerseke, NL (seaside)	116		160		160	115	116
Arbon, CH (alpine)	–		75		110	–	–
Horgen, CH (urban)	–		–		–	140	150

*The data of Perseke[26] refer to the sampling periods of August 1979 to August 1980 and September 1980 to August 1981, resp., and are therefore not strictly comparable to the data of our institute. **The rainwater samples were taken with an open sampler and could therefore be contaminated by dustfall.

rainwater in a rural region (Jülich) and a region with metallurgical industry (Stolberg) was performed by our institute in 1983[32]. The concentrations are well balanced and their yearly average values correspond to 6 mg SO_4/l, 3 mg NO_3/l and 1.6 mg Cl/l which lie in the ranges given by Georgii[6] i.e. 3.0–6.6 mg SO_4/l, 1.8–3.5 mg NO_3/l and 0.6–5.0 mg Cl/l.

The almost equal concentrations in these two different regions indicate that the greater part of these anions or their precursors, SO_2 and NO_x, is transported and distributed from the major emission zones over extended distances by the air masses. A comparison of the cationic and anionic composition of rain water in the region studied is shown in figure 11. From this it becomes possible to estimate what proportion of these anions are of anthropogenic origin. The average monthly concentrations of Na^+ and Cl– have almost the same pattern. This is an indication that the Na^+ and Cl– ions dissolved in rain water originate from the sea. If the ratio of the Na^+ to Cl– concentrations in the sea is compared to that in rain water and the marine origin of the total Na^+ content in rain water is assumed, it can be concluded that 90% of the Cl^+ originate also from the sea on a yearly average. Analogous calculations show that $< 10\%$ of the SO_4^{2-} is of marine origin and the rest is of anthropogenic origin, whereas the NO_3^- is totally of anthropogenic origin.

† Deceased (May 12th, 1985).

Acknowledgment. The authors are grateful to 'Deutscher Wetterdienst' (German Meteorological Service), UBA Berlin (German Environmental Protection Agency), the Section of Analyt. Chemistry at the University Dortmund, the Institute of Biogeography of the University Saarbrücken, the Delta Institute, Yerseke, and local authorities at Goslar, Arbon and Horgen for their technical support in the operation of stations of the sampler network. The supply of meteorological data by the German Meteorological Service in Essen is gratefully acknowledged.

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