Nr. 7

The quality of precipitation in an industrial area

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1. Aims and methods

The chemical compounds, which appear in almost countless number and contribute to the pollution of the atmosphere, can be related to groups of different pollutants (KUTTLER 1979 b), of which sulphur and nitrogen compounds are most important ones.

The distribution and concentration of particular pollutants is based on meteorological, location and time factors. Beside these given differences it is possible to compare the concentrations of a 'polluted' and an 'unpolluted' atmosphere exemplarily, as it is shown in table 1 (KUTTLER 1980). The high increase of pollutants in polluted air becomes obvious especially for the concentrations of SO_2, CO and the content of dust.

After the release from different groups of sources the pollutants are subject to the different mechanisms of chemical change (compare i.e. BEILKE 1980, GIEBEL 1977, GEORGII & HERRMANN 1979), dilution as well as deposition. Beside the chemical mechanisms of decomposition two different ways for the removal of impurities from the atmosphere can be distinguished: This is on the one hand the way of dry deposition and on the other hand the way of wet deposition. While during the dry deposition the pollutants are deposited on the various surfaces exposed to the atmosphere and are even absorbed or assimilated by the stomata of plants, wet deposition results from the transfer of pollutants by the different forms of precipitation.

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Table 1

Comparison between an "unpolluted" and a "polluted" atmosphere (from KUTTLER 1980)

Pollutant	unpolluted	polluted	Enrichment factor (polluted/unpolluted)
dust	0,01 - 0,02 mg/m^3	0,07 - 0,7 mg/m^3	7 - 35
sulphurdioxide	0,001 - 0,01 mg/m^3	0,05 - 5,2 mg/m^3	50 - 520
carbondioxide	310 - 330 ppm	350 - 700 ppm	1,1 - 2,1
carbonmonoxide	1 ppm	5 - 200 ppm	5 - 200
nitricoxide	0,001 - 0,01 ppm	0,01 - 0,1 ppm	10
hydrocarbon (total)	1 ppm	2 - 20 ppm	2 - 20

Estimations of the dry deposition are difficult to make, for numerous parameters have an influence on the specific deposition velocities of the different pollutants. GEORGII and others(1980) have carried out calculations on this matter for different pollutants, as well as PERSEKE and others (1980) for the impact per unit area of sulphur in the Federal Republic of Germany and KUTTLER (1981) the same for the Central Ruhr District, Northrhine-Westphalia, FRG.

It is much easier to determine the wet deposition. Since May, 1978, the water of rainfall, which is collected weekly in open "bulk-samples" (see MILLER & MILLER 1980), has been analysed on the content of sulphate calcium and chloride in the Central Ruhr District as the investigation area. In addition the pH-value and the amount of precipitation is determined. For some time we are additionally analysing the water of single rainfall events in a parallel investigation in order to determine the enrichment factor for bulk-samples (see MOLDAN 1980).

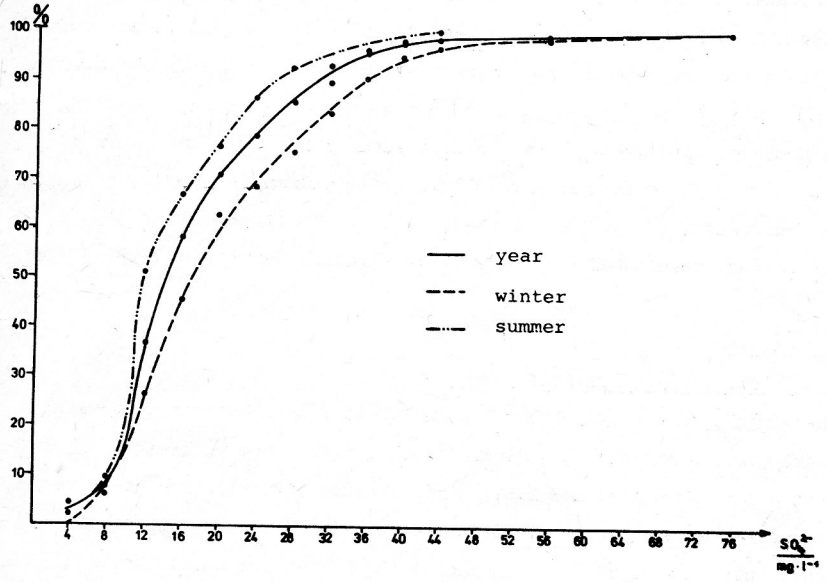
Preliminary results of a two-year investigation period can be presented.

2. Results

2.1 Sulphate concentrations

The monthly values of sulphate pollution have been calculated from the weekly values and showed a clear seasonal difference with higher concentrations in winter and lower summer values (fig. 1). The distribution of cumulative frequency reveals a median value of 15 mg sulphate/liter, the 10 per cent value is about 9 mg/l and the 90 per cent value at 31 mg/l. In the summer half-year we had a median value of 12 mg/l with a 10 per cent value at 8 mg/l and a 90 per cent value at 26 mg/l. In the winter half-year we had higher sulphate concentrations on the contrary. 50 per cent of the sum values reached 17 mg/l, 10 per cent of the values did not exceed 9 mg/l and 90 per cent of the values were lower than or equal to 36 mg/l. Beside the seasonal differences of sulphate concen-

Fig. 1 Cumulative frequency of sulphate concentrations in precipitation (May 1978 - April 1980)



trations we also found a dependence of these concentrations on the specific amount of precipitation. The results are shown in figure 2. The concentrations are calculated as arithmetic mean values of 5 mm precipitation and it becomes clear that the high sulphate concentrations in precipitation appear in low rainfall amounts while low sulphate concentrations are found in high precipitation values.
For an increase from 5 to 55 mm precipitation per week - the elevenfold value - sulphate pollution sank to about one third of the concentration. The reasons for this are the variability of rainfall intensity (general rain - shower) and the different velocity of fall resulting from the size of the raindrops (GEORGII 1965).
The lowest concentrations had been measured in July, 1979 with values of about 1 mg sulphate/liter. The reason for this was a western weather condition during which the dominance of tropic air masses caused heavy showers. The highest sulphate concentrations had been measured after a long dry period with about 75 mg/l in January, 1979. During the dominance of this stable weather condition an SO_2-smog (KUTTLER 1979 a) had developed in the lower atmospheric layer and led to the call out of a regional smog-alarm in the western Ruhr District. The rainfall after this dry period caused an extensive cleaning of the atmosphere.

2.2 Calcium

Even this pollutant showed a seasonal difference with relatively low values in winter and spring and slightly higher values in summer and fall (see figure 3). Referring to the mean value of 3.2 mg calcium/l summer values showed an increase by 11 per cent while the values measured in the winter half-year decreased by 18 per cent. For calcium is an essential part of atmospheric dust and is mainly used in the building and construction trade these higher summer values can possibly be inter-

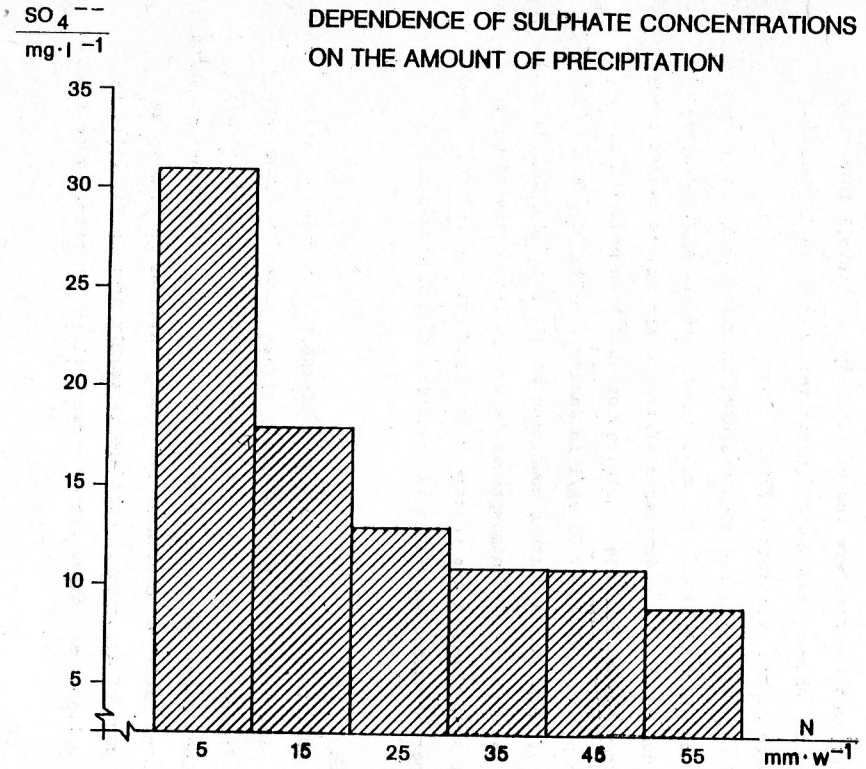
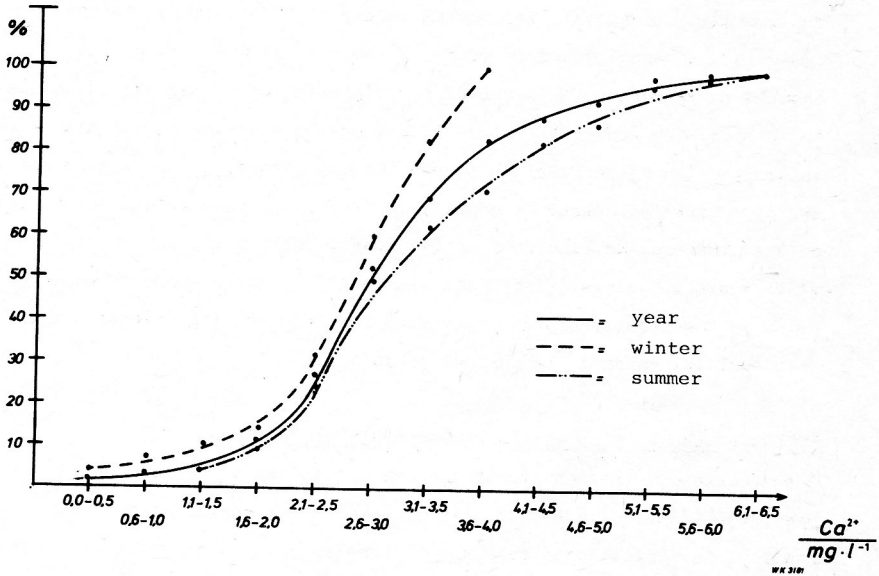


Fig. 2 Dependence of sulphate concentrations on the amount of precipitation

Fig. 3 Cumulative frequency of calcium concentrations in precipitation (May 1978 - April 1980)



preted as a result from the intense building activities.

2.3 Chloride

The chloride concentrations did not show any seasonal difference according to the preliminary results. The arithmetic mean value of chloride concentrations amounted to 4.4 mg chloride/l, while the measured concentrations ranged between 1 and 15 mg chloride/l (see figure 4).

2.4 pH-values

The arithmetic mean value of the pH-values of precipitation reached 4.3 with an average range between 3.8 and 5.1. Figure 5 shows the cumulative frequency of pH-values in precipitation during the investigated period. The groups show the differences between the annual mean values and the values for the respective half-years. In the winter and spring months the degree of acidity in precipitation exceeded the values of the other months. The fact of these seasonally differing values was still shown by others (KAYSER and others 1974). These higher winter acidity is generally explained by the increased heating intensity and the resulting emission of various pollutants.

3. Comparison of the results with a clean air station

A comparison of the results of the concentrations of pollutants in precipitation between Bochum station (industrial region) and other stations is difficult to realize, because on the one hand the examinated periods are seldom comparable, and on the other hand because of the different methods of analysis of the different investigators. For the integration of the Bochum results the measured values have been compared to those of a clean air station (Brótjacklriegel, Bavarian Forest,

Fig. 4 Cumulative frequency of chloride concentrations in precipitation (May 1978 - April 1980)

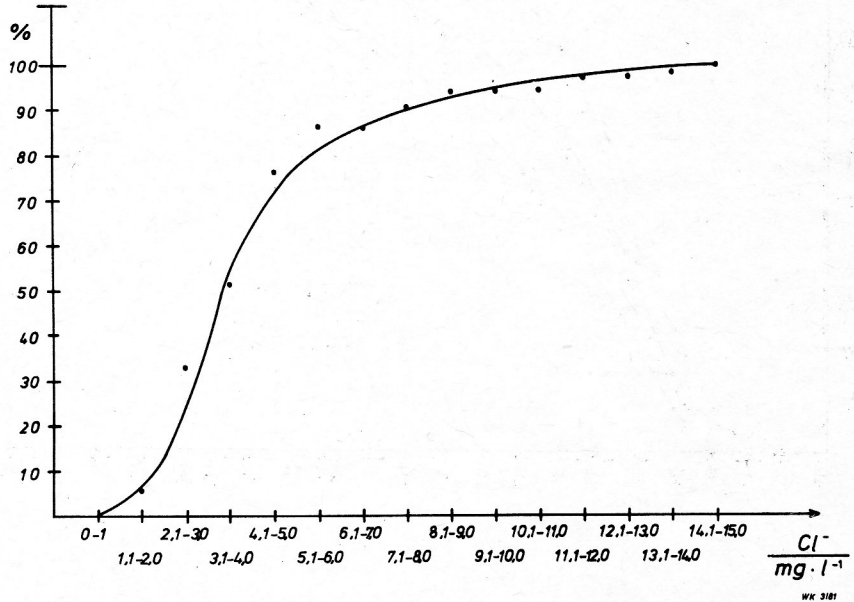
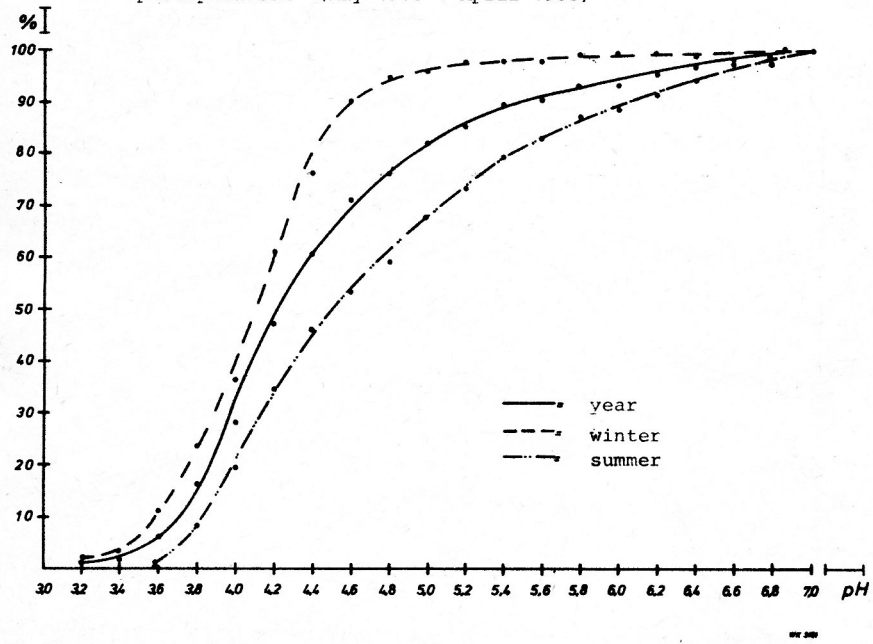


Fig. 5 Cumulative frequency of pH-values in precipitation (May 1978 - April 1980)



FRG). The material of this station was taken from the book of measured values "Luftqualität 1980, Meßnetz des Umweltbundesamtes", of pilot station Schauinsland, 1981. As table 2 shows, the values of Bochum station exceed those of the clean air station several times. The only exception are the pH-values which do not show any difference at both stations. A comparison of the amount of pollutants transferred to the soil reveals the higher impact of an industrial station (table 3). An analysis of results from different industrial regions shows values which can be compared to those of Bochum station, however, the values are partly higher at Bochum (see LIKENS and others 1979).

4. Effects

The impact of pollutants which are deposited either in the dry or wet way can be noticed in the whole spectrum of ecosystems. From the number of investigations on this matter I'll choose two examples which I consider as most important and explain them exemplarily, and these are the acidification of soils in Northrhine-Westphalia and the damage to the buildings.

In the frame of extended soil investigations it was possible for BUTZKE (1981) to show that the pH-value has decreased in all examinated soil profiles. Table 4 shows a résumé of the measured values according to which this process of acidification of the soil is not limited to single certain ecosystems, but can be found in all the investigated soil types with different vegetation and humous forms. The comparison of the pH-values of the analysed soil samples showed a pH-reduction from 0,12 to 1,15 units during the 20-year period.

However, it is not only nature which is damaged by acid rain, but also buildings created by man reveal a permanently increasing susceptibility

Table 2

CONCENTRATIONS OF POLLUTANTS, pH-VALUES AND ELECTRIC CONDUCTIVITY
at a polluted and unpolluted station

	$\frac{SO_4^{2-}}{mg \cdot l^{-1}}$	$\frac{Ca^{2+}}{mg \cdot l^{-1}}$	$\frac{Cl^-}{mg \cdot l^{-1}}$	pH	$\frac{\text{el. cond.}}{\mu S \cdot cm^{-1}}$
I. polluted Station [1) 2)] (Bochum)	18,6	3,20	4,40	4,30	55 [4)]
II. unpolluted Station [3)] (Brotjacklriegel)	3,6	0,36	0,49	4,25	25,7
ratio I. : II.	5,2	8,90	8,90	-	2,1

[1)] bulk-samples; May 1978 to April 1980

[2)] without consideration of enrichment factor C_{bulk}/C_{pure}

[3)] bulk-samples; January 1980 to December 1980

[4)] March 1981 to January 1982

Table 3

DEPOSITION OF POLLUTANTS AT A POLLUTED AND UNPOLLUTED STATION

(in kg · ha^{-1} · $year^{-1}$)

	SO_4^{2-}	Ca^{2+}	Cl^-
I. polluted Station [1] (Bochum)	104	23	32
II. unpolluted Station [2] (Brotjacklriegel)	36	3,6	5,0
ratio I. : II.	2,9	6,4	6,4

[1] January to December 1979;
yearly amount of precipitation: 732 mm

[2] January to December 1980;
yearly amount of precipitation: 1004 mm

Table 4

ACIDIFICATION OF DIFFERENT SURFACE SOILS IN NORTH RHINE-WESTPHALIA

during a 20-year period (values after a figure of BUTZKE 1981)

pH-value range of examined soils 1959/61		2,5 - 2,9	3,0 - 3,4	3,5 - 3,9	4,0 - 4,9	5,0 - 5,4
amount of pH-value reduction (1959/61 to 1981)		0,12	0,34	0,50	0,67	1,15
number of examined soils		9	11	10	3	2
types of soils		Podzols (7) Podzol-Pseudogley (1) Black Plaggen soils (1)	Brown Earths/ Gray-brown podzolic soils (3) Ranker-Podzol (1) Pseudogleys (6) Black Plaggen soils (1)	Brown Earths/ Gray-brown podzolic soils (3) Pseudogleys (5) Gray-brown Plaggen soils (2)	Pseudogleys from marl (2) Gley (1)	Pseudogleys rich in bases from marl (2)
prevailing vegetation	deciduous tree	(3)	(6)	(9)	(3)	(2)
	scotch pine	(3)	(3)	(1)	-	-
	spruce	(3)	(2)	-	-	-
humus types	mull	-	-	(5)	(3)	(2)
	mould/mull	-	(3)	(3)	-	-
	mould	(2)	(3)	(2)	-	-
	vegetable mould	(1)	(3)	-	-	-
	humus	(6)	(2)	-	-	-

Table 5

Damage of concrete by different degrees of acid precipitation (after DIN 4030)

	weak damage	strong damage	very strong damage
pH-value	6,5 - 5,5	5,5 - 4,5	< 4,5

to this environmental problem. Especially sand- and limestone as well as concrete buildings are corroded considerably by this aggressive rainwater. Detailed investigations had been carried out by LUCKAT (1976, 1978). These investigations demonstrate the high damage rate of sandstone buildings (i.e. the Dome of Cologne) in the Rhine-Ruhr-Region. For a long time civil engineers have pointed to the damage to concrete buildings (see i.e. RUFFERT, 1981), and called it a certain "concrete aggressiveness of precipitation", what is additionally shown in the values of table 5.

So this classification reveals the considerably damaging influence of acid rain with pH-values below 4.5 - as it is collected at Bochum station.

Summary

Pollutants emitted by various sources are removed from the atmosphere by way of dry and wet deposition. It is difficult to estimate the extent of dry deposition of pollutants, because the specific deposition velocities of the various pollutants are influenced by different parameters. On the other hand, it is easier to measure pollutants which are transported to the ground by differnt forms of precipitation.

At Bochum station, in the Central Ruhr District, North-Rhine Westphalia FRG, such investigations have been carried out since 1978 and are still running. Precipitation is collected in open collectors and weekly analysed on the contents of sulphate, calcium, chloride and ammonium, and the pH-value is determined at the same time. Preliminary results of a two-year investigation period can be presented.

The sulphate concentrations reached an average of about 18 mg sulphate/l. The concentrations of this pollutant reached higher values in winter than in summer half-year, just as during persistent rain compared to shower precipitation. For the content of calcium a mean value of 3.2 mg of calcium/l was determined with higher values in winter than in summer. The chloride concentrations showed an artihmetic mean value of 4.4 mg chloride per liter without any seasonal difference. The pH-values of this station amounted to 4.3 with lower winter values (4.0) compared with the summer period (4.5). A comparison of concentrations of pollutants transferred to the ground (station of an industrial region to a station of a clean air region) shows that we find higher concentrations at the station in the industrial region, where three times as much sulphate and six times the amount of calcium and chloride reach the ground. This increased influx of pollutants into the soils leads to a long-term decrease of pH-values in the surface soils of Northrhine-Westphalia and to an increased erosion of sacred sandstone and profane concrete buildings.

Résumé

Les corps polluants qui ont été émis de différentes sources sont éliminés de l'atmosphère soit par la voie d'un dépôt sec, soit par la voie d'un dépot humide. Il s'avère difficile d'évaluer l'étendue des dépôt secs des polluants car différents paramètres influencent la vitesse des dépôts specifiques aux polluants. Par contre il est plus facile de mesurer les polluants qui arrivent sur terre sous les différentes formes de précipitations. Ceci est expérimenté depuis 1978 à la station de Bochum, NRW, RFA. Chaque semaine des prélèvements de ces précipitations sont recueillis dans des réservoires et analysés pour leur contenu en sulfate, calcium et chlorure et on détermine la valeur du pH. On peut après deux années de recherches, donner quelques résultats préliminaires. Les concentrations moyennes en sulfate étaient de l'ordre de 18 mg de sulfate/l. Les concentrations de ce corps polluant étaient durant le semestre d'hiver plus élevées que durant le semstre d'été. On observait la même comparison entre les pluies continues et les averses. Pour la teneur en calcium on pouvait établir un ordre moyen de 3,2 mg calcium/l avec des ordres plus importants en été qu'en hiver. La concentration en chlorure montrait un ordre arithmétique moyen de 4,4 mg de chlorure/l mais ne présentait aucune différence saisonnière. La valeur du pH était à la station de 4,3 et montrait en hiver un ordre (4,0) moins important qu'en été (4,5).

Une comparaison des quantités des corps polluants au niveau du sol (station dans une région industrielle - station dans une région d'air pur) montre de facon évidente que dans les régions industrielles arrivent au sol trois fois plus de sulfats, six fois plus de calcium et de chlorure. Cette augmentation des corps polluants arrivent au niveau du sol conduit à une diminution à long terme de la valeur du pH des sols en surface du NRW et conduit de la même facon à une érosion accélérée des constructions religieuses en gré et des constructions profanes en béton.

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