INPUT OF ATMOSPHERIC POLLUTANTS IN A REMOTE HIGHLAND AREA

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ABSTRACT. In North Rhine-Westphalia, FRG, measurements of dry and wet depositions of the chemical constituents sulphate, chloride, nitrate, fluoride, calcium and ammonium were made in a remote highland (Sauerland, Rhenish Slate Mountains) and in an industrial area (Ruhr District). The measurements were carried out at 16 bulk-sampler stations and at two places with dry/wet samplers. Moreover the immission rates of sulphur and nitrogen compounds, either in the form of gas and particles, were determined. At the mountain station (845 m above sea-level) additional measurements concerning the wet deposition, dependent on the wind direction and the concentration of aerosol particles (for sulphate, nitrate and chloride) could be made. Estimations concerning wash-out and rain-out are given, as well as the percentages of the most important shares of acid-forming anions in the precipitation.

1. INTRODUCTION

For the registration of the immission and deposition structure of selected pollutants in the densely wooded, rural area 'Sauerland' (Rhenish Slate Mountains, North Rhine-Westphalia), dependent on space and time, measurements were made at 16 places between 1982 and 1984.

The area under investigation has an extent of 4,500 km^2, is predominantly covered by coniferous forests, between 300 m and 845 m above sea-level, and divided by numerous small rivers. In the valleys there are smallholdings, and here and there small industrial enterprises.

The data obtained in this area are compared to results obtained at the Bochum station in the industrial area. Fig. 1 shows the location of the measuring stations.

Bulk-samplers (SAM = surface active monitoring; after RUMPEL o.J.) were used as sampling stations, from which samples of the total monthly precipitation were taken; in addition these devices were equipped with filters, which allowed to determine the immission rate of sulphur and nitrogen compounds in the form of gas and particles (additional information in FUKUI 1966, KUTTLER 1985).

Additionally wet- and dry only samplers were installed on the highest mountain of the area under investigation (845 m above sea-level,

H.-W. Georgii (ed.), Atmospheric Pollutants in Forest Areas, 89–100.

Kahler Asten; in the following called 'mountain station') and in the industrial area station (located in the Botanical Garden of Ruhr-University Bochum), to obtain samples of the diurnal total of precipitation.

Moreover, these two samplers allowed to measure the deposited dust and - with the sampler at the mountain station only - suspended dust particles.

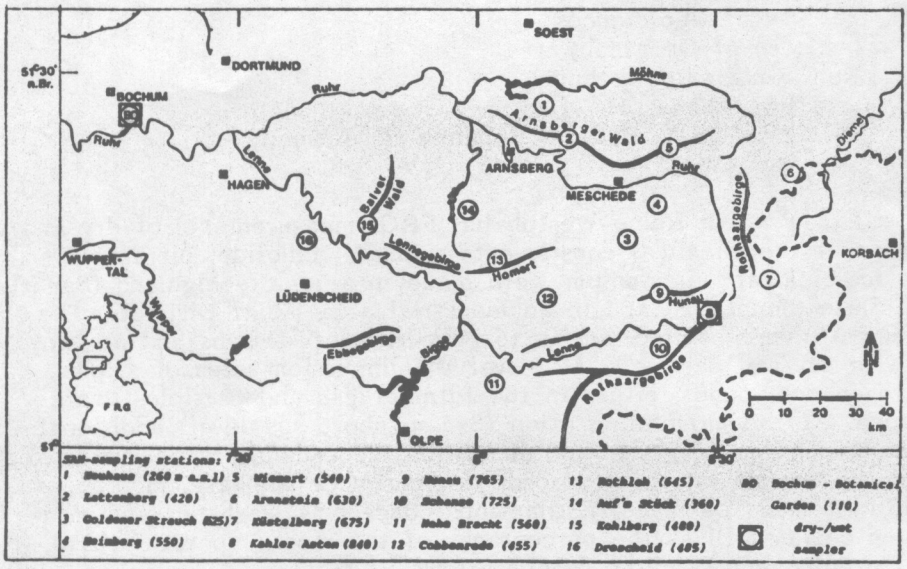

Fig. 1 Location of the measuring stations in the area unter investigation (Sauerland, North Rhine-Westphalia, FRG)

2. RESULTS OF THE MEASUREMENTS

2.1 Immission Rates

A survey about the spatial distribution of the immission rates of sulphur and nitrogen is given in fig. 2 and fig. 3.

The spatially limited character of the average sulphur-immission rates showed - for an ecologically unloaded area - a relatively high ratio of 1:4.6 between the place with the lowest deposition ($\bar{x}$ = 3.08 mg/m² · d at station 5) and that with the highest deposition ($\bar{x}$ = 14.31 mg/m² · d).

The spatial distribution of the average nitrogen immission rates (fig. 3) varies between 0.13 mg/m² · d (station 5) and 0.49 mg/m² · d (station 13). The ratio is 1:3.8. In general, a correlation coefficient of r = 0.94 (r^2 = 0.88) means a high correspondence between the average rates of the nitrogen and sulphur immission rates (exception: station 2, whose values were not taken into consideration, since there the sulphur rates were relatively high due to the emissions from the stack of a near small industrial source; cf. KUTTLER 1985).

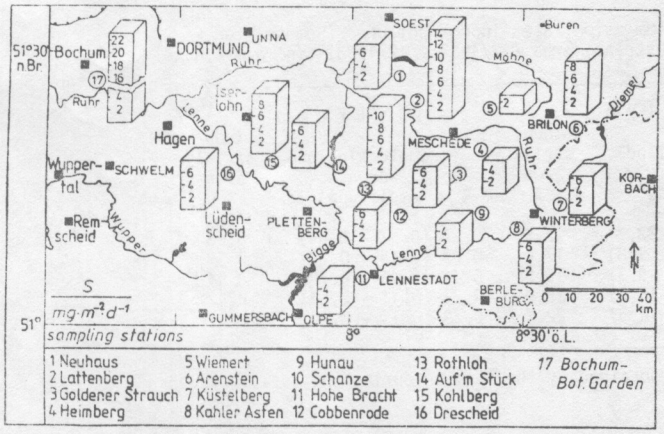

Fig. 2 Average values of sulphur immission rates in the remote highland area (Sauerland) and at Bochum station (industrial area) (12/1982 - 12/1983)

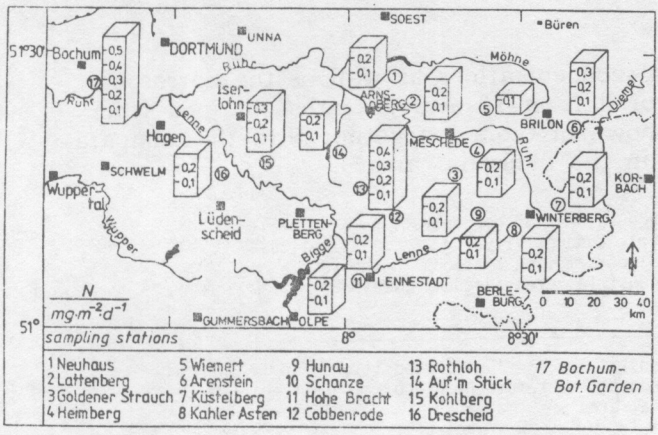

Fig. 3 Average values of nitrogen immission rates in the remote highland area (Sauerland) and at Bochum station (industrial area) (12/1982 - 12/1983)

Table 1 shows the seasonal differentiation of the immission rates.

In autumn and winter the sulphur immission at the stations in the remote highland as well as at the stations in the industrial area were higher than in spring and summer. During the winter months the regional average of the non polluted region was almost twice as high as the spring/summer average; this applies also to the station in the industrial area, where the rate is, however, three times higher.

The variation of the rates (lowest and highest annual average) for the individual season makes clear that even in the so-called non polluted regions relatively great differences in the immission structure - spatially and temporally - can be noticed; from the bioclimatic point of view this is an important aspect e.g. for the planning of health resorts. The highest values for nitrogen were recorded in summer, the lowest rates in autumn and winter. The seasonally adjusted values of the industrial area were twice as high as those of the non polluted region.

In contrast to the sulphur immissions, which vary especially in winter (1:5), the nitrogen immissions reached their peak level mainly in summer (1:6).

Tab 1. Sulphur and nitrogen immission rates in non polluted (remote highland area) and polluted (industrial) area (12/1982 - 12/1983) (in mg/m²· d)

season	sulphur		nitrogen	
	remote highland area $\bar{x}$ amplitude[1)]	industrial area $\bar{x}$	remote highland area $\bar{x}$ amplitude[1)]	industrial area $\bar{x}$
winter	10,97 (4,7 - 23,7)	32,7	0,22 (0,17 - 0,34)	0,58
spring	5,41 (2,8 - 9,8)	17,6	0,29 (0,13 - 0,39)	0,53
summer	5,65 (2,8 - 9,3)	15,5	0,41 (0,13 - 0,78)	0,94
autumn	7,93 (2,3 - 16,0)	25,0	0,22 (0,11 - 0,53)	0,42
average	7,51 (3,1 - 14,3)	22,7	0,29 (0,13 - 0,49)	0,62

[1)] highest and lowest average obtained by the station during the total measuring period

2.2 'bulk' - precipitation

The regional average of 'bulk'-concentrations as well as the corresponding 'bulk'-depositions (computed from 16 average rates obtained from the measuring stations) are shown in table 2 together with the comparative figures from the station in the industrial area.

Tab. 2. Weighted 'regional average values' of concentrations (in mg/l), of the pH-value and of the electric conductivity (in µ S/cm) as well as average depositions (in mg/m²· d) of sampling stations in the remote highland area (Sauerland) and industrial area (Bochum) (12/1982 - 12/1983)

	'bulk'-concentrations			'bulk'-depositions		
	remote highland area $\bar{x}$	rel.dev. (%)	industrial area $\bar{x}$	remote highland area $\bar{x}$	rel.dev. (%)	industrial area $\bar{x}$
pH	4,22	2,6	4,24	-	-	-
electr. Cond.	43,00	16,1	58,00	-	-	-
$SO_4^{=}$ - S	1,64	17,7	2,56	4,81	13,3	5,80
NO_3^{-} - N	0,64	17,6	0,85	1,89	17,5	1,89
Cl^{-}	1,62	19,5	2,93	4,62	28,2	6,97
F^{-}	0,117	35,9	0,178	0,339	34,5	0,404

While the pH-average rates of the polluted and non polluted area hardly differ, the concentration rates for sulphate exceed the rates of the non polluted area by 56 %, those for nitrate by 33 %, those for chloride by 124 %, and those for fluoride by 52 %.

In the non polluted highland area the variations in relation to the regional average were less than 20 %; only for fluoride a higher rate of 36 % rel.dev. was found.

The values for the deposition rates show that compared to the industrial area rates in the non polluted area are either the same (in case of nitrate) or higher.

E.g. for sulphur (approx. 21 %), chloride (approx. 51 %) and fluoride (approx. 19 %). It must, however, be considered that the annual

total precipitation in the clean air region is generally higher than in the industrial area.

In the non polluted area the deposition rates varies between 13 % and 28 % from the regional average value. Only the deviations of the fluoride input reaches 24 %.

2.3 'wet- and dry-only' samples

As far as 'wet-only'-concentrations are concerned it can be stated that the concentrations in rainwater measured by the mountain station differ considerably from those measured by the industrial area station (tab. 3).

Tab. 3. 50 %-percentages of 'wet-only' concentrations measured at a mountain station in the non polluted highland area (Kahler Asten, 845 m a.s.l.) and a station in the industrial area (Bochum, 140 m a.s.l.) (1/1983 - 2/1984)

	pH	el.Cond. (µS/cm)	SO_4^{2-}-S (mg/l)	NO_3^--N (mg/l)	NH_4^+-N (mg/l)	Cl^- (mg/l)	Ca^{2+} (mg/l)
industrial area	4,15	55,0	2,3	0,64	1,30	2,0	1,40
mountain station	4,17	30,0	1,2	0,44	0,81	0,8	0,42

To determine the frequency distribution of the concentration in the precipitation (for sulphate) at the mountain station and in the industrial area the sulphate concentrations (C) measured in the diurnal precipitation samples were compared to the thus computed average concentrations ($\overline{C}$). The figures obtained were subjected to a frequency distribution (fig. 4).

In this context cf. SMITH (1983), who defined an episode of short, but high load with the arbitrarily fixed 3 C-rate (= triple concentration of the average rate $\overline{C}$).

The results obtained here show that a 3 C-rate occurs in 1.5 % of all cases at the mountain station and in 2.5 % of all cases at the industrial area station.

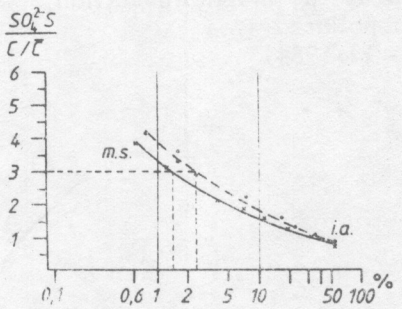

Fig. 4 Ratios between SO_4^{2-} - S concentration of diurnal precipitation samples (C) and the average rates ($\overline{C}$) computed thereof for the station in the industrial area and for the mountain station (1/1983 - 2/1984)

SMITH (1983) found that in Norway this rate is exceeded in 7 % of all cases.

The wet-only depositions are neither evenly distributed within the year nor within the month, but vary in some cases extremely in the first line due to the varying amount of precipitation, and secondly due to the varying concentrations of chemical constituents in the precipitation.

These temporally different records can result in a stress for the ecological systems, especially in the forests.

For sulfate, for example, therefore either the monthly percentage of deposition with regard to the total deposition during the measuring period and the daily maximum records were computed (fig. 5).

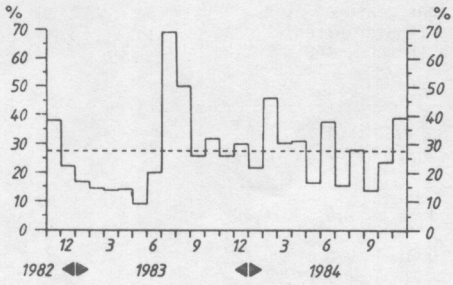

Fig. 5 Maximum diurnal share of SO_4^{2-} - S depositions of the monthly 'wet-only' total deposition during the measuring period at the mountain station in the non polluted area (11/1982 - 11/1984)

The average daily maximum sulphate-sulphur deposition - expressed in percentage of the monthly total - was 27.4 %.

The highest diurnal maximum was 70 % of the monthly deposition in July 1983. Extremely high deposition rates occur in connexion with short heavy showers.

Also from month to month you can record - referring to the deposition rate of the total measuring period - extremely varying figures due to the 'wet-only'-deposition (fig. 6).

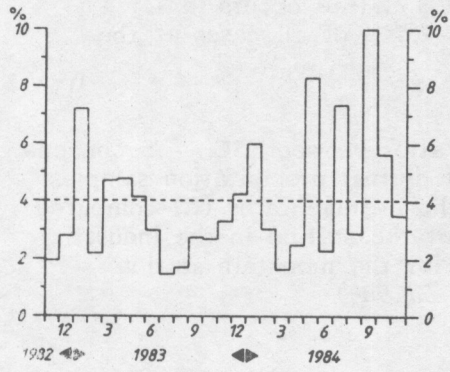

Fig. 6 Monthly percentage of SO_4^{2-} - S deposition of the 'wet-only' total deposition during the measuring period at the mountain station in the non polluted area (11/1982 - 11/1984)

So on one hand extremely high rates (10 % of the total deposition during the measuring period), and on the other hand extremely low rates (2 %) were obtained.

2.3.1 'Wet-only'-inputs depending on the wind direction. To determine the input of pollutants depending on rain-bringing wind directions the precipitations collected with the wet and dry only sampler on a diurnal basis at the non polluted mountain station were compared to the diurnal average of the eight main (surface-) wind directions. The results for the chemical constituents sulphate and chloride shall be explained (for further constituents cf. KUTTLER 1985).

From fig. 7 can be seen that the sulphate-sulphur concentrations dependent on the wind direction show no significant differences between the individual sectors; on the average the concentrations vary between 1.4 mg/l for precipitation from southwest and slightly higher values of 2 mg/l for precipitation from east and northeast.

A completely different distribution was recorded for the chloride concentration in the precipitation. The highest rates were obtained from rain-bringing winds coming from northwest (2.4 mg/l). Concentrations in the precipitation from the sector north-east to south showed the significantly low values of 0.5 to 0.6 mg/l.

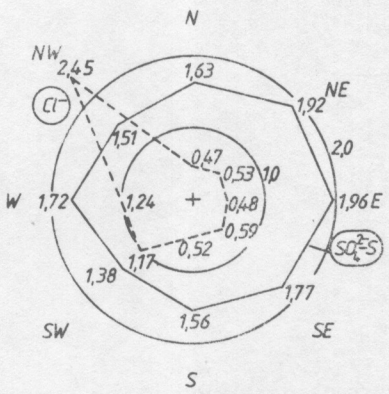

Fig. 7 Distribution of the weighted concentrations in rain dependent on the wind direction for SO_4^{2-} - S and Cl^- (in mg/l) at the mountain station in the non polluted area (11/1982 - 11/1984)

Fig. 8 shows the average chloride and sulphate-sulphur deposition rates for each sector. Sulphate reached the highest average in the east-sector. The reason is that only a few, but very heavy showers within the framework of some Vb-weather situations caused the high deposition rates.

In the case of chloride, however, the winds from northwest dominate with 31.4 mg/m² · d. The sectors north, east and south are obviously underrepresented: the input of particles from these directions showed rates of 3.1 to 7.9 mg/m² · d of chloride.

Compared to the total measuring period (11/1982 - 11/1984) - due to the main rain-bringing directions west and southwest - more than 65 % of the particles were recorded from these sectors.

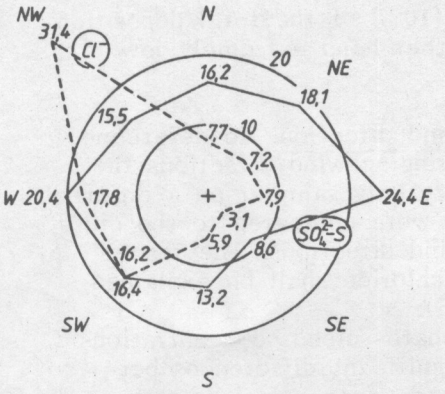

Fig. 8 Distribution of wet deposition dependent on the wind direction for SO_4^{2-}- S and Cl^- (in mg/m²·d) at the mountain station in the non polluted area (11/1982 - 11/1984)

2.3.2 Aerosol Concentrations. Aerosol concentrations of sulphate, nitrate and chloride particles were measured at the mountain station by means of a membrane and a teflon-filter (pore size 0.45 µm) respectively 0.2 µm) with an average suction rate of 1 m³ /d for a period of 14 days. The individual data can be seen in table 4.

Tab. 4. Means of aerosolconcentrations at the mountain station in the remote highland area (Kahler Asten, 845 m a.s.l.) (in µg/m³) (11/1982 - 11/1984)

	$\bar{x}$	max.	min.	rel.dev. (%)	n
SO_4^{2-}-S	1,25	2,77	0,23	0,61	50
NO_3^-- N	0,35	0,75	0,01	0,22	48
Cl^-	0,28	0,83	0,01	0,23	52

The course of the suspended dust concentrations described in fig. 9, shows the highest aerosol concentrations for sulphate with 2.3 µ g/m³ in July 1983, the lowest concentrations were recorded in winter, especially in December 1983 with 0.35 µ g/m³. Nitrate showed high monthly averages in March 1983 with 0.61 µ g/m³, June 1983 (0.55 µ g/m³), March 1984 (0.54 µ g/m³), and September (0.50 µ g/m³). The lowest concentrations were found in October 1983 (0.04 µg/m³) and December 1983 (0.08 µg/m³).

The monthly average value for chloride varied between 0.56 µg/m³ October 1984) and 0.06 µg/m³ (February 1984).

2.3.3 Comparison of the total deposition ('wet and dry-only') between polluted and non polluted area. Table 5 contains the complete dry plus wet (however, not the gaseous one) deposition of sulphate, nitrate and chloride particles for the station in the non polluted high-

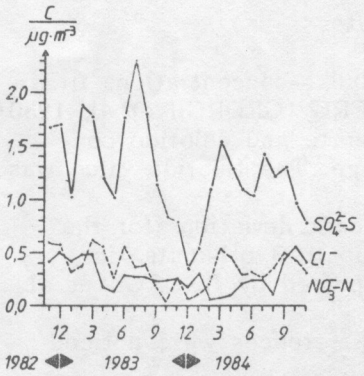

Fig. 9 Monthly average of aerosol-concentration at the mountain station in the non polluted area (11/1982 - 11/1984)

Tab. 5. Total deposition and percentage of dry deposition at the station in the industrial area (Bochum) and at the mountain station (Kahler Asten (in mg/m² · d) (1/1983 - 2/1984)

	SO_4^{2-} - S			NO_3^- - N			Cl^-		
	$\bar{x}$	$\bar{x}$(dry) (%)	rel.dev. (dry) (%)	$\bar{x}$	$\bar{x}$(dry) (%)	rel.dev. (dry) (%)	$\bar{x}$	$\bar{x}$(dry) (%)	rel.dev. (dry) (%)
mountain station	7,26	21,8	9,4	2,35	20,3	11,8	6,18	15,5	12,9
industrial area	6,60	34,1	16,3	1,93	26,8	18,2	5,14	29,2	15,5
m.s. - i.a.	0,66	-12,3	-6,9	0,42	-6,5	-6,4	1,04	-13,7	-2,6

land area as well as for the station in the industrial area.

The mountain station shows values which are for sulphate 10 % higher than the rates at the station in the industrial area. For nitrate the rates are 22 % higher, for chloride 20 % higher. All values apply to the total deposition.

While at the mountain station the shares of dry deposition are 15.5 % and 21.8 %, these rates are distinctly higher in the polluted area, where the share of dry deposition is 26.8 % to 34.1 %.

Besides the fact that the dry deposition in the non polluted region plays a less important part, the standard deviation of the dry depositions compared to their average values show that the occurrence of the above mentioned suspended particles in that area is subject to less deviations than in the polluted area.

3. DISCUSSION OF THE RESULTS

The Sauerland region, the remote highland area under investigation, receives pollutants predominantly from the long-distance transport, with the exception of some small industrial sources in the valleys.

3.1 'bulk'-precipitation values and immission rates

The computed regional average values of the 'bulk'-concentrations fit into the scheme of other rural regions in the FRG (GEORGII et al. 1980).

The spatial variability of the sulphate, nitrate and chloride concentrations was nearly 20 % apply to the average. The fluoride value was higher due to an industrial plant in the area.

The average pH-values show only insignificant deviations for the acid end of the scale, but greater deviations (up to 3 pH-units) for the basic end. Similarly high amplitudes are reported by GEORGII et al. (1982).

Essentially greater spatial and temporal differences were noticed for the immission rates (SAM-stations).

Besides the greater variability of the sulphur-immission rates in the Sauerland in winter the absolute rates in the cold season are twice as high as in summer. The reasons for this are on one hand the increasing demand for heat and the resulting higher SO_2-emissions near the ground due to the dropping temperatures, and on the other hand the increasing occurence of weather situations with almost low exchange conditions.

Since the immission rate is made up of the immission concentration and the run of the wind it cannot be decided, whether high or low concentrations or low respectively high wind speeds are responsible for the immission rate determined by the measuring station, without measuring the wind speed.

To my opinion it is not permissible to conclude from the immission rate to the immission concentration, as SCHUH (1985) did.

3.2 'wet and dry'-only values

The dry and wet deposition measured in the industrial area and in the highland area seperately correspond to those obtained in other slightly loaded areas of the FRG (PERSEKE 1982).

The most distinct annual curve is shown for the chloride concentrations with maximum values in winter and low rates in summer. One reason for the higher chloride concentrations in winter might be the frequent occurence of rain-bringing west winds from the sea; the partly occuring summer maxima of the sulphate concentrations might be explained by the higher photochemical production rate during the summer months, which produces more sulphur in this period.

The greatest dependence of the concentration of chemical constituents in precipitation on the wind direction in the non polluted region was shown by chloride with high concentrations in the case of precipitation from northwest; for continental precipitation from the east, however, the lowest concentration was recorded. Since either the North Sea and the Ruhr District are situated in the westnorthwest of the mountain station it cannot be cleared up exactly, where this increase in concentration can be put down to.

As the examinations at the industrial area station for chloride, dependent on air-massis and wind direction, also show a clear increase in the concentration from the northwest sector (results of an earlier

unpublished paper of the author), - and thus show that they are influenced by the sea - this may also be true for the mountain station.

Comparative measurements concerning the problem of 'rain-out' and 'wash-out' between industrial area station and mountain station (845 m above sea-level) revealed that the precipitation sum measured in the industrial area was 56 % of that registered at the mountain station, with the share of sulphate being 77 %, of nitrate being 71 % and of ammonium as well as chloride being 91 % of the share at the mountain station. Compared to the lower amount of precipitation in the industrial area higher inputs were recorded.

Supposing that the greatest share of the wet deposition at the slightly loaded mountain station mainly results from the 'rain-out', the deposition measured at the station in the industrial area (140 m above sea-level) result from the 'wash-out' of the 700 m thick airmass between the mountain station in the non polluted region and the station in the industrial area. After various measurements in Frankfurt/M. and on the small Feldberg/Taunus (GEORGII 1965) similar results were obtained, with the exception of the slightly deviating rate for sulphate; the same result was obtained for the 'wash-out' shares in the Soviet Union with 45 % to 78 % (PETRENCHUK & SELEZNEVA 1970).

From the data available (aerosol concentration and deposition rates) the deposition velocity for sulphate (v_d = 1.4 cm/sec), nitrate (v_d = 1.6 cm/sec.) and for chloride (v_d = 4.5 cm/sec) were computed.

The deposition rates of nitrate and chloride - the rate for sulphate corresponds to that measured by EVRETT et al. (cit. in DAVIES & NICHOLSON 1982) - are higher than those determined in the laboratory (compilation of individual values in PERSEKE 1982).

Concerning the question of the percentage of the most important acid-forming anions in the precipitation it can be stated that at the measuring station in the polluted area and at the station in the non polluted area more than 50 % fall to sulphate ions; at the station in the industrial area chloride ions rank second with 26 %, then follow the nitrate ions which make 19 %. At the mountain station, however, nitrate is second before chloride; responsible for the higher share of chloride in the industrial area are probably the shorter distance between the sampling station and the sea, but also the release of HCl caused by industrial processes.

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