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Investigations on tropospheric
wash-out

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Technical (Final)-Report

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Abstract

This report summarizes the results of chemical analyses of individual cases of precipitation sampled at different locations. The locations showed a great variety with respect to altitude, climate and level of industrial and anthropogeneous pollution.

Furthermore detailed analyses and continuous records of the trace-substance concentration during individual rainfalls are discussed. The variations of the concentration during the course of the rain and their relations to quantity, intensity and types of rain as well as to meteorological parameters, are discussed.

Finally, preliminary studies on the incorporation of trace-substances into cloud- and rain-drops are presented, indicating the relative importance of rainout compared to washout.

Introduction

Cloud- and rain-elements are of great importance for the removal of trace-substances-aerosols and gas-traces - from the atmosphere. The continuous increase of anthropogeneous and industrial emissions into the atmosphere in many parts of the world but also the presence of radioactive aerosols lead to the question of the mechanism responsible for the transport of these trace-substances from the atmosphere back to the ground. This problem is also important for considerations on the budget of trace-substances in troposphere and stratosphere.

These questions lead to the problem of investigating rainout and washout of trace-substances. Rainout is active within clouds during cloud-formation and coalescence of drops while washout is active below the cloud-base. Both processes influence considerably the tropospheric residence-time of aerosols and trace-gases.

As introduction we want to present a schematic survey indicating the major sources and sinks of atmospheric trace-substances and their qualitative budget in the troposphere.

The majority of trace-substances are formed at the earth- and the ocean-surface.

Fig. 1 gives a survey showing the following processes responsible for the formation of gases:

- a) Emissions from the interior of the earth, the earth surface, the ocean surface
- b) Microbiological processes
- c) Wood-fires
- d) Volcanic eruptions
- e) Assimilation of plants
- f) Reactions in the atmosphere

The following additional processes lead to the formation of aerosol-particles:

- a) Formation at the earth- or oceanic surface
- b) Combustion processes
- c) Exhalation of pine forests
- d) Formation from the gas-phase.

Vertical wind-distribution and convective processes in the boundary-layer carry the trace-substances aloft into higher layers. This leads to a more and more even distribution of the concentration with altitude. The general circulation of the atmosphere favours the horizontal transport. The main sinks are absorption at the earth surface, uptake by vegetation and animals, sedimentation and coagulation of particles and last but not least incorporation of trace-substances into cloud- and rain droplets.

Neglecting horizontal transports we can write the budget-equation for atmospheric trace-substances after Junge (1) in the following form:

$$K \left(\frac{\partial^2 n}{\partial z^2} \right) - an - bn^2 - v \left(\frac{\partial n}{\partial z} \right) = 0$$

with: K = turbulent Diffusionskoeffizient (cm^2/sec)

n = particle-concentration (cm^{-3})

a = washout coefficient (sec^{-1})

b = coagulation constant (cm^3/sec)

v = sedimentation velocity (cm/sec)

z = altitude (cm)

The first term describes the distribution of trace-substances by turbulent mixing, the second term the removal of trace-substances from the atmosphere by rainout and washout, the third term coagulation-process and the last term the sedimentation in the gravity-field of the earth. After these introductory remarks we will now deal with rainout and washout.

The mechanism of rainout and washout

If we consider the effect of sedimentation and coagulation as of secondary importance compared to washout, we can write the budget-equation in the following form:

$$K \left(\frac{\partial^2 n}{\partial z^2} \right) = an \rightarrow n = n_0 e^{-\sqrt{a/K} z}$$

This is probably justified up to altitudes of 5 kms. Measurements of the trace-gas concentration which were recently carried out by Jost (2) resulted in K -values of 5×10^4 to $1 \times 10^5 \text{cm}^2/\text{sec}$ for altitudes up to 2 kms.

With these K -values, we can calculate a tropospheric residence-time of about 10 days on the basis of the tropospheric distribution of Aitken-nuclei as measured by Weickmann (3). For SO_2 the measurements by

Georgii and Jost resulted in a tropospheric residence-time of 4-6 days. This seems to be the right order of magnitude and shows that rainout and washout are of great importance for the removal of aerosols and gases from the atmosphere.

In Fig. 2 we present a schematic survey on the different processes leading to the incorporation of trace-substances into cloud- and rain-elements. We have to distinct between processes effective within the cloud, summarized generally as rainout and those effective below the cloud base during the fall of the rain-elements through the cloud free zone, referred to as washout. Besides the incorporation of aerosols we have to consider the absorption of gaseous traces, the concentration of which is often about five to fifty times higher than that of the comparable components in aerosols.

A certain number of aerosol particles is consumed as condensation nuclei during the first stage of cloud-formation. Only particles of a certain size-range will act as condensation-nuclei. According to the investigations by Yamamoto and Ohtake (4) and by Kuroiwa (5) the fraction of particles active as condensation nuclei becomes smaller with decreasing size. The following figures are given by the above-mentioned authors:

	Radius in micron				
	0.1-0.2	0.2-0.4	0.4-0.6	0.6-1	1-2
	Percentage of particles activated				
Yamamoto & Ohtake	0.4	2	17	60	100
Kuroiwa	0.2	1.7	15	24	100

This table shows that only the giant particles are fully consumed as condensation nuclei.

On the other hand particles larger than $10/\mu$ radius can be neglected for the processes discussed here since they are removed from the atmosphere by dry fallout.

Theoretical considerations on rainout and washout

It can be generally stated that the mechanism of rainout and washout is extremely complex. Its rate of efficiency depends on the following parameters:

- a) Particle-size and concentration of the aerosols present in the atmosphere
- b) Size and number of collecting droplets
- c) Mass of soluble components in the aerosols and the chance of chemical reaction in the droplets
- d) Absorption from the gas-phase and irreversible incorporation of the gaseous components in the cloud- and raindrop
- e) Supply of liquid water by condensation during lifting of cloud-droplets
- f) Increase of the concentration in the droplets caused by partial evaporation during the fall below the cloud-base.

The concentration of trace-substances in rain as measured at the ground is in first approximation proportional to the total supply of trace-substances into the clouds, inversely proportional to the liquid water content of the clouds and proportional to the partial evaporation of droplets.

Following Junge (6) we can write

$$K_r = \frac{\epsilon c}{L}$$

c = concentration of trace-substances in $\mu\text{g}/\text{m}^3$
 L = liquid water content in gr/m^3

$0 < \epsilon \leq 1$ = rainout coefficient

$$\epsilon = \epsilon_n + \epsilon_b + \epsilon_f$$

ϵ_n = consumption of condensation nuclei
 ϵ_b = attachment of particles by Brownian motion
 ϵ_f = attachment of particles by Facy effect

Exact values for ϵ as well as for ϵ_n , ϵ_b and ϵ_f are not known. The following approximations are valid:

$$\epsilon_n = 0.01 - 0.9 \quad \text{according to particle-size and to composition of particles.}$$

$$E_c = 0.01 - 1.0$$

according to particle-size. The coefficient of attachment increases with decreasing size of the particles according to the theory by Smoluchowski. For particles below 0.1μ , E_c is nearly 1.0.

$$E_r \approx 0.01$$

In this connection attention is directed to our discussion in Annual Rep. No. 3, 1962. According to Goldsmith, Delafield and Cox (7) the Facy-effect is very ineffective.

According to these assumptions the concentration of trace-substances in rainwater, incorporated by the effect of rainout should be independant of the quantity of rain. It will be shown in a later chapter of this report that these assumptions are confirmed by measurements. Before we go into details with respect to rainout, our theoretical considerations will be extended to the washout process.

The total concentration of trace-substances in rain incorporated by rainout and washout can be written as:

$$K = K_r + fK_w$$

The factor $f \geq 1$ indicates the increase of concentration due to partial evaporation.

The amount of trace-substances removed from the atmosphere by washout is equal:

$$C_w = \int_0^h \int_S c N_w E_c dh dS$$

$$N_w = N \pi r^2$$

N_w = number of raindrops

r = radius of raindrops

h = distance from the earth surface to the cloud base

Δ = time of fall

E_c = collection coefficient.

Substituting the concentration of trace-substances between ground and cloud-base

$$S = \int_0^h c dh$$

and

$$\alpha = NT r^2 E_c$$

we receive:

$$C_w = S e^{-\alpha} (1 - e^{-\alpha R})$$

for the total amount of trace-substances which will be removed by wash-out. Consequently, we receive for the concentration K_w which will accumulate in rainwater by wash out when the quantity R of rain falls:

$$R = \frac{4}{3} \bar{r}^3 NT$$

= quantity of rain

T = duration of rain

$$K_w = \frac{S}{R} \left(1 - e^{-\frac{3RE_c}{4r}} \right)$$

For large quantities of rain the exponential term becomes less important and the concentration of trace-substances in rain becomes inversely proportional to the amount of rainfall. This is also confirmed by measurements.

Comparison with actual measurements is very difficult since E_c and S are not well known. Particularly a separation of the effect of rainout and washout is difficult. In a later chapter some results regarding this problem will be presented.

The coefficient of efficiency of washout depends also on the particle-size of the atmospheric aerosols but as well on the ratio: droplet size of raindrops to particle-size of aerosol-particles. The following approximate values can be assumed:

$$\begin{aligned} E_c &= 1 && \text{for particles larger than } 10 \mu \\ &0.5 && \text{for particles larger than } 5 \mu \\ &0.2 && \text{for particles larger than } 2 \mu \end{aligned}$$

Besides aerosols, trace gases are being incorporated into cloud and precipitation-elements. It is evident, that only such gases are of interest in this connection which react with other partners in cloud-water. In this connection the reaction of NH_3 and SO_2 in cloud-droplets has to be mentioned which was recently investigated by Mason and

van den Henvel (8). This reaction is of great consequence for the subsequent formation of $(NH_4)_2SO_4$ after evaporation of the droplets.

Estimations on rainout

In order to calculate the concentration of atmospheric trace-substances incorporated into cloud-elements we follow W. Jacobi (9) in his computations on the incorporation of radioactive aerosols into cloud-droplets. He based his computation on a droplet-size distribution for Stratus according to Houghton (10) and for Cumulus-clouds according to aufm Kampe (11). The droplet-size distribution is presented in Fig. 3.

If we assume the life-time of a Cumulus-cloud being 1 hour and if we assume under the application of the Smoluchowski-theory, the absorption-coefficient being 1.0 we find that within one hour

- 93 % of the particles of the size: $r = 10^{-6}$ cm
- 10 % of the particles of the size: $r = 10^{-5}$ cm

are attached to the cloud elements. However we have to bear in mind that only particles larger than 10^{-5} cm radius increase the substance in the droplet considerably.

In a Stratus-cloud the same percentage of attachment of particles of the atmospheric aerosols is reached only after 2 1/2 hours (Fig. 3).

The increase of substance in the droplets caused by the incorporation of condensation nuclei and the attachment of particles can be calculated in the following way: The quantity of substance incorporated by a condensation nuclei of $r = 10^{-4}$ cm, which is completely soluble is about 3 to 6 x 10^{-12} gr according to density. If the radius is only 5×10^{-5} cm the quantity of substance incorporated amounts from 6×10^{-13} gr to 1.2×10^{-12} gr. For the Cumulus-cloud the following parameters are valid:

- Liquid water contents: 4 gr/m³
- Average droplet radius: $\bar{r} = 20 \mu$
- Number of droplets: 120/ccm

Aerosol-concentration in cloud-level (assumed):

$$r = 10^{-6} \text{ cm: } 3000/\text{ccm}$$

$$r = 10^{-5} \text{ cm: } 1000/\text{ccm}$$

Quantity of substance:

$$(r = 10^{-6} \text{ cm}) N = 3000/\text{ccm} \quad 1.2 \times 10^{-14} \text{ gr/ccm to } 2 \times 10^{-14} \text{ gr/ccm}$$

$$(r = 10^{-5} \text{ cm}) N = 1000/\text{ccm} \quad 4 \times 10^{-12} \text{ gr/ccm to } 8 \times 10^{-12} \text{ gr/ccm}$$

Particles of 10^{-6} cm are completely attached to the cloud droplets within 1 hour. The contribution of substance to each of the 120 droplets/ccm is about 1.7×10^{-17} gr per droplet.

10 % of particles of 10^{-5} cm radius are attached to cloud droplets within 1 hour. That means 100 particles are attached to 100 of the 120 droplets. The contribution of substance is about 4×10^{-15} gr per droplet.

Comparing these figures with those of substance brought into the droplets by condensation we see that the contribution of rainout is small.

We can furthermore assume that 10 % of the total substance of the aerosols consists of sulfate. Then, rainout contributes 4×10^{-16} gr SO_4^{--} to each droplet.

With an average radius of 20μ , 10^{11} droplets form 1 ltr of cloud water. Our estimates show that rainout contributes 0.3 mg substance or 0.03 mg SO_4^{--} to each litre of cloud water while during condensation 8 to 50 mg SO_4^{--} /ltr had been incorporated into the cloud water. These rough figures suggest that the condensation process is of greater importance for atmospheric chemistry than rainout. Under optimum condition, in the presence of a large number of large particles the amount of substance incorporated by rainout may be equal to that incorporated by the condensation nuclei.

We are now going to extend these considerations to the incorporation of gaseous traces into cloud droplets. Measurements of the concentration of gas traces by aircraft ascents were carried out recently for the first time (Jost (2)). In the course of these investigations we found that the

average SO_2 -concentration in 3000 mtrs altitude is about $10 \mu\text{g}/\text{m}^3$ equal $10^{-11} \text{gr}/\text{cm}^3$. In a cloud with a droplet concentration of 120/ccm an amount of $8.4 \times 10^{-14} \text{gr SO}_2$ could be incorporated in each droplet under the assumption of the incorporation efficiency being 1. This would mean that in 10^{11} droplets = 1 ltr. cloud water $8.4 \times 10^{-3} \text{gr SO}_2$ equal $1.3 \times 10^{-2} \text{gr SO}_4^{--}$ would be incorporated.

We cannot expect that the absorption efficiency of gases into droplets is 1.0 but also if we assume a collection efficiency of only 0.1 the amount of SO_2 incorporated will still be $8 \times 10^{-5} \text{gr SO}_2$ per droplet and is therefore higher by a factor of 10 compared with the substance incorporated by aerosols.

Incorporation of trace-gases leads therefore to an increase of the SO_4 -concentration in cloud water by 1.3 mg/ltr. This seems quite plausible. Therefore the gas phase must not be disregarded concerning its importance for the transfer of substance into cloud-elements by rainout. Quantitative data on the efficiency of incorporation of gas-traces into cloud- and rain elements are completely missing. Laboratory experiments in this direction are carried out by the authors of this report presently.

With regard to the efficiency of washout below the cloud-base it must be mentioned that its efficiency is influenced very much by the vertical distribution of atmospheric trace-substances as well as by drop-size distribution, particle size distribution of the aerosols and intensity of rainfall. The importance of washout for the total concentration of trace substance in rainwater will increase in areas with high pollution leading to an accumulation of trace-substances near the ground. Experimental results on the order of magnitude of the washout coefficient for trace-gases are not known. Measurements under atmospheric conditions are very difficult to carry out owing to the heavy fluctuation of the different parameters. We have therefore started laboratory experiments, using the setup shown in Fig. 4. A mixture of pure air and air containing a constant and known concentration of a trace-gas (SO_2 , NH_3 , NO_2 or others) will be drawn through a rainout-chamber holding $1,5 \text{ m}^3$ air. The gas-concentration will be checked before entering the chamber and

after leaving the chamber. Inside the chamber a continuous "rain" of droplets of known size will reduce the gas-concentration by washout. Besides checking the gas-concentration, the accumulation of substance in the water used for the "artificial rain" in the chamber will be continuously measured. From the data received in this way, the absorption coefficient for gases can be determined.

Objectives of the present investigation

The previous statements show clearly that the mechanism of rainout and washout is very complex indeed and depends on a large number of different physical and chemical parameters. The investigations described in this report had the objective to separate the different processes by experimental methods. It therefore appeared sensible to deal with the following questions:

- 1) What is the contribution of rainout i.e. of the processes taking place within the cloud and of washout i.e. of the processes taking place below the cloud base during the fall of raindrops, to the total concentration of trace-substances in precipitation?
- 2) What is the contribution of gaseous traces and of aerosols to the total concentration of trace-substances in precipitation?
- 3) Does there exist a relation between quantity and/or intensity of precipitation and the concentration of trace-substances in rainwater?
- 4) In what way does the concentration of trace-substances fluctuate during the course of rain in individual rainfalls?
- 5) How important is partial evaporation of falling raindrops for the concentration of trace-substances in rainwater measured at the ground?

The chemical composition of individual rainfalls

Within the frame of the present investigation chemical analyses of individual rainfalls were carried out at several locations in different altitudes and in regions with a different level of pollution. These investigations were carried out at the following locations during the periods of time stated:

Frankfurt/M - Department of Meteorology (1956-1957, 1960-1962)
Taunusobservatory on Mt. Kleiner Feldberg, 800 mtrs altitude (1950-1957, 1960-1961)
Zugspitz observatory, Bavarian Alps, 2966 mtrs. altitude (1957, 1958, 1961-1962)
St. Moritz, Switzerland, 1800 mtrs. altitude (1960, 1961)
Mt. Corviglia, near St. Moritz, 2500 mtrs. altitude (1961)
Island of Capreia in the Mediterreanean Sea (1962).

During summer 1963 and summer 1964 chemical analyses were carried at four stations in Austria in different altitude but at a very short horizontal distance. These four stations are located:

Innsbruck - Department of Meteorology	530 mtrs. altitude
Hungerburg	830 mtrs. altitude
Seegrube	1800 mtrs. altitude
Hafelekar	2300 mtrs. altitude

The investigation at these stations are related to our research on the budget of trace-substances in rain.

Methods of Analysis

The precipitation was sampled in specially designed raingauges made of glass. The dimensions of these were in agreement with the standard rain-gauge of the German Weather Service. Funnels and sampling-glasses were cleaned daily with distilled water. After sampling, the rainwater was filtered but not concentrated. The analysis of the different compounds

was carried out according to the instructions described in our Annual Report No 1, July 1960.

NH₄: The NH₄-concentration was determined by adding 1 ml of Nessler reagent and 1 ml of a solution of Seignette salt to 10 ml rainwater. The resulting color was compared in a Eppendorf photometer with those of standard-solutions.

NO₂: The NO₂-concentration was determined in a similar way by adding 1 ml reagent Griess-Ilosvay to 10 ml rainwater.

NO₃: For the determination of the nitrate component the rainwater was treated with sulfuric acid and chloroform solution of Brucin-alkaloid. The concentration was measured by comparing with standards.

SO₄: For determination of the SO₄-concentration the slightly changed analysis-method by Kelly and Rogers was applied. The turbidity of the solution was measured in the Eppendorf-photometer after attaching a nephelometer.

Na, Ca, K were determined by flame-photometric analysis applying an Eppendorf-flame photometer.

Besides the determination of the above mentioned components it was of importance to measure the acidity of rainwater, the pH-value and the electrolytical conductivity. For discontinuous measurements of pH-value, we used an pH-meter type WTW-39N and for discontinuous measurements of electrolytical conductivity an instrument type WTW-LBR.

The electrolytical conductivity of rainwater is a good indicator for the total concentration of ions and by this for the total concentration of inorganic compounds dissolved in rainwater.

Parallel investigations of the electrolytical conductivity and the sum of cations (NH₄⁺ + Na⁺ + Ca⁺⁺) resp. the sum of anions (SO₄⁻⁻ + Cl⁻⁻ + NO₃⁻⁻) analyzed separately show that there exists a strong correlation between analysis and measurement of the conductivity. This correlation

holds for three locations where we collected individual rainwater samples from April 1961 to March 1962. Fig. 5 shows the correlation between electrolytical conductivity and ions analyzed in rainwater. A certain range of fluctuation must be expected since the ions analyzed are only a limited selection of the total number of components dissolved in rainwater. It must also be expected that the range of fluctuation increases with increasing electrolytical conductivity.

Generally the electrolytical conductivity (κ) is the inverse value of the resistance

$$R = \frac{1}{\kappa} \frac{l}{q} (\kappa \text{ in } \mu\text{S/cm})$$

l is the distance of the electrodes, q the size of the electrodes. These are instrument-constants. The electrolytical conductivity depends furthermore of:

- 1) the concentration of ions in the solution
- 2) the mobility of ions
- 3) the electric charge which is carried by each ion
- 4) the temperature and the viscosity of the solution

The concentration of ions depends on the quantity of matter dissolved and coefficient of dissociation a

$$a = \frac{\text{number of ions}}{\text{number of molecules dissolved}}$$

The so-called Ostwald-law determines the relation between quantity of the dissolved matter and grade of dissociation with the understanding that very dilute solutions have a high grade of dissociation. As an example 0.001 molar solutions of HCl, H₂SO₄, HNO₃, KCl, NaCl, (NH₄)₂SO₄ have a dissociation-coefficient of 0.9 or above. For the ion-concentration to be expected in rainwater the coefficient of dissociation is close to 1.0.

The electrolytical conductivity can be written in the following way:

$$\kappa = \sum n_+ u_+ + \sum n_- u_- \quad \begin{array}{l} n = \text{number of ions} \\ u = \text{mobility of ions} \end{array}$$

The following table shows the concentrations of different ions in mg/l equivalent of an electrolytical conductivity of 1 μ S/cm.

m (mg/l)	NO_3^-	Cl^-	$\frac{1}{2}\text{CO}_3^{--}$	$\frac{1}{2}\text{SO}_4^{--}$	Na^+	$\frac{1}{2}\text{Ca}^{++}$	NH_4^+	K^+
	1.0	0.54	0.43	0.63	0.53	0.38	0.28	0.60

These values are taken from a paper by Sikana (12). Owing to their high mobility the concentration of Hydrogenions deserves special attention since a concentration of only 0.0032 mg/l H^+ is equivalent 1 μ S/cm. The relation between pH-value and electrolytical conductivity is laid down in Fig. 6. The values given therein are valid for a temperature of 18°C. Since the mobility of ions depends of the temperature, temperature influences the electrolytical conductivity. The mobility is also inversely proportional to the radius of ions. This is the cause for the fact that different ions furnish differing contributions to the total electrolytical conductivity of a solution.

Results of measurements

The chemical analysis of the concentration of trace-substances in precipitation during 1956 and 1957 in Frankfurt/M showed the following results:

We found as average of 89 individual rainfalls:

NH_4	NO_3	NO_2	SO_4	Cl
3.8	3.6	0.2	15.0	5.4 mg/l

Details were given in our Annual Report No 1, July 1960. As already mentioned similar analyses were carried out in Frankfurt/Main during 1960 and 1961. As average of 138 individual analyses we received the following data:

NH_4	NO_3	SO_4	Cl	Na	Ca	
3.2	2.8	16.3	3.9	1.1	1.9 mg/l	\mathcal{R} 63.4 μ S/cm

During 1960 and 1961 the same type of investigation was carried out at Langen, a small town about 20 kms from Frankfurt. The average values out of 50 individual cases are:

NH ₄	NO ₃	SO ₄	Cl	Na	Ca		Σ
3.9	2.6	15.3	6.7	1.1	1.4	mg/l	45 μS/cm

From March to December 1957 66 analyses of individual rainfalls were carried out on Taunus observatory on, Mt. Kleiner Feldberg. The average values are the following:

Average of quantity of rain	NH ₄	NO ₃	SO ₄	Cl	
9.8 mm	1.6	2.1	5.3	1.8	mg/l

Details were given in Annual Rep. No 1, July 1960. These measurements were repeated during 1960. The following average values were gained as the result of the analysis of 91 cases:

NH ₄	NO ₃	SO ₄	Na	Ca		Σ
1.4	2.6	4.5	1.3	1.2	mg/l	38.5 μS/cm

On the summit of the Zugspitze 13 analyses of precipitation were carried out during summer 1957. During 1960 to 1962 within the frame of a larger research-program 156 analyses of individual rainfalls were performed. Details of this alpine program were published by Georgii & Weber (13) as well as by Weber (14).

The average result of the 13 measurements made during summer 1957 is:

Average of quantity of rain	NH ₄	NO ₃	SO ₄	Cl	
7.5 mm	1.0	0.8	2.7	1.6	mg/l

The average result of 156 measurements made during 1960 to 1962 is:

NH ₄	NO ₃	SO ₄	Na	Ca		Σ
1.2	0.8	1.5	1.1	1.6	mg/l	44 μS/cm

When we normalize the results gained at Frankfurt during 1957 and during 1960/61 in the following way that the Frankfurt-results are equal 1.0 we receive the following relations:

	NH ₄	NO ₃	SO ₄	Cl	Na	Ca	Σ
Frankfurt/M 1957 resp. 1960 to 1961	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Taunus observatory 1957 measurements	0.45	0.48	0.36	0.34	-	-	-
1960/61 measurements	0.34	0.93	0.27	-	1.2	0.63	0.60

Even under the consideration that the total amount of precipitation on the Taunus ridge is nearly twice the amount measured in Frankfurt, the relative concentration of trace-substances in rainwater in Frankfurt is also considerably higher when calculated on the basis of assumed equal amounts of rainwater at both stations. The NH₄- and NO₃-concentration on the Taunus ridge is about 20 % lower than at Frankfurt, the SO₄- and Cl-concentrations are 35 % to 40 % lower. From these results it can be assumed that the additional portion of trace-substances measured at Frankfurt/M must have been incorporated into the rain elements in the air layer between 800 mtrs. altitude and the Main valley in 100 mtrs. altitude.

Relation Frankfurt - Taunus observatory - Zugspitze

During summer 1957 measurements of chemical constituents in rainwater were carried out at the above-mentioned three stations simultaneously.

If we normalize the concentration of trace-substances found in precipitation in that way that the Frankfurt-concentration is equal 1, the following relations are found:

	NH ₄	NO ₃	SO ₄	Cl
Frankfurt/M	1.0	1.0	1.0	1.0
Taunus observatory	0.57	0.71	0.42	0.40
Zugspitze	0.37	0.20	0.26	0.29

The figures show a further decrease in concentration from the Taunus observatory to the Zugspitze. It can be assumed that the concentration on the Zugspitze represents more or less that of larger cloud-elements since the summit of Zugspitze is within clouds when it rains.

Relations between atmospheric trace-substances and the chemistry of precipitation

In a recent paper (Georgii (15)) we have compared simultaneous measurements of gaseous traces, aerosols and chemical constituents of rainwater. This research was carried out at four locations in different altitudes (Frankfurt/M, altitude: 100 mtrs., Taunus observatory, altitude: 800 mtrs., St. Moritz/Switzerland: altitude 1800 mtrs. and Zugspitze, German Alps, altitude: 2960 mtrs.). It must however be mentioned that the horizontal distance from Frankfurt to the alpine stations is considerable. Therefore an exact comparison of the results gained at these four stations is not possible. The following summary of the results is only a more schematic survey. We have plotted in Fig. 7a and 7b a vertical distribution of the concentration of NH_4^- and NO_3^- -components analyzed in rain, in aerosols and as trace-gas. We have also entered the number of large nuclei (dashed line). The concentration is entered in a logarithmic scale, the altitude in a linear scale. Fig. 7a shows that the decrease of NH_4^- in aerosols follows an exponential function and parallels the decrease of the number of particles. This results permit the conclusion that the NH_4^- -concentration is distributed equally in the aerosol-particles, independent of the altitude. This is a further indication for the general presence of NH_4^- in the continental aerosols. S and W indicate the range of fluctuation between summer and winter. The following fact is also of importance. The decrease of gaseous NH_3 and of the NH_4^- -concentration in rain run almost parallel. With respect to the NO_3^- -distribution Fig. 7b shows that between Frankfurt, Taunus observatory and St. Moritz the decrease of the concentration in aerosols is proportional to the decrease of numbers of particles. In contrast to that on the Zugspitze a higher concentration was found. The concentration of

gaseous NO_2 is also higher on the Zugspitze than at St. Moritz.

This is in agreement with results gained by Weber (14) that the trace-substance concentration is generally higher north of the main ridge of the Alps than south of the alps. Intensive precipitation in the luv of the alps contribute to a decrease of concentration.

The relatively constant vertical distribution of gas traces in higher layers of the troposphere has important consequences for precipitation-chemistry. The significance lies in the fact, that the supply of gaseous traces is greater than that of aerosol-particles in layers where the formation of precipitation takes place.

Aircraft ascents of the vertical distribution of SO_2 and NO_2 up to 6000 mtrs. showed that in altitudes above 2000 mtrs. the concentration does not decrease very much but remains more or less constant (Jost (2)). Investigations carried out by Junge in Hawaii (16) came to similar results. Also Junge found a much stronger decrease of the aerosols compared with that of the trace-gases. According to these findings the importance of trace-gases increases with increasing altitude.

On the distribution of different components in rainwater

Ratio NH_4/SO_4

According to Junge (6) a considerable portion of the continental aerosol-particles consists of $(\text{NH}_4)_2\text{SO}_4$. According to van den Heuvel and Mason (8) ammonium -sulfate particles can be formed when water droplets evaporate which had been exposed to air containing gaseous sulfur-dioxide and ammonia. It is therefore suggested that the concentration of SO_4 and NH_4 in cloud- and raindrops is directly related to the capture of ammonium-sulfate particles or to the gasphase-diffusion, followed by chemical reaction at the surface of the droplet and diffusion in the liquid phase.

As result of our measurements we found the following NH_4/SO_4 ratios in rainwater:

Frankfurt/Main:	$\text{NH}_4 = 0.25 \text{ SO}_4$
Taunus observatory:	$\text{NH}_4 = 0.32 \text{ SO}_4$
Zugspitze	$\text{NH}_4 = 0.37 \text{ SO}_4$
theoretical $(\text{NH}_4)_2\text{SO}_4$:	$\text{NH}_4 = 0.37 \text{ SO}_4$

In unpolluted areas the ratio $\text{NH}_4 : \text{SO}_4$ is in good agreement with the ratio to be expected in $(\text{NH}_4)_2\text{SO}_4$. In polluted areas SO_4 is in surplus concentration due to the sulfur production by human activity.

Ratio NO_3/SO_4

The SO_4 surplus found in precipitation in polluted areas becomes also evident when we consider the ratio NO_3/SO_4 . We can presuppose that NO_3 is not a pollutant to the same extent as SO_4 . Comparing the ratio NO_3/SO_4 in precipitation and in aerosols we find that the fraction of NO_3 increases in rain and in aerosols from polluted to unpolluted areas

<u>location</u>	<u>NO_3/SO_4 in precipitation</u>	<u>NO_3/SO_4 in aerosols</u>
Frankfurt - winter	0.16	0.17
Frankfurt - summer	0.41	0.23
Taunus observatory	0.40	0.44
Zugspitze	0.53	0.36
St. Moritz	0.90	0.66

The low SO_4 -content in precipitation in St. Moritz is remarkable.

Concentration of trace-substances in continuous rain and showers

A distinction of all cases of precipitation in showers and cases of continuous rain (connected with slow up-slide motion in the atmosphere) shows the following results: In this evaluation we have only considered cases with more than 2 mms. rain. Furthermore we have normalized the

cases of the two categories to equal quantities of precipitation in order to exclude differences of the trace-substance concentration due to different quantities of rain. The average values for the period July 1956 to December 1957 are given below:

Type of precipitation	average quantity of rain in mms	Concentration in mg/ltr.				Nos. of cases
		NH ₄	NO ₃	SO ₄	Cl	
shower	11.3	2.3	2.3	7.2	2.0	21
continuous rain	11.3	2.2	2.1	13.4	1.7	44

Fig. 8 shows the results. In the case of NH₄, NO₃ and Cl there exists practically no difference between the two types of precipitation. In the case of SO₄ the concentration in continuous rain is nearly twice the concentration in showers.

Continuous rain has generally less intensity than showers. Investigations of the droplet size of rain produced in layer-clouds show a diameter in the range 0.2 to 1.2 mms. The average drop-size in showers is however 2 to 3 mms. The high SO₄-concentration can certainly be explained by the slow fall-velocity of small drops and their longer residence time in the ground-layer of the atmosphere with its high level of sulfur pollution. The other components analyzed are much more even distributed within the atmosphere and not accumulated within the ground-layer as the sulfur-component is. Therefore a longer residence of the drops in the ground-layer is not so effective with respect of increasing the concentration of the other components in the drops.

The effect of dry periods on the concentration of trace-substances in rain

In order to evaluate the influence of the supply of trace-substances in the atmosphere on the concentration of the same components in precipitation we have distributed the cases of rainfall analyzed in Frankfurt and

~~on the Taunus observatory from January to December 1957 according to the following view-point:~~

Group I : contains cases of rainfall after a period of at least 3 dry days previous to the rainfall concerned

Group II : contains cases of rainfall after a period of not more than 12 hours without rain previous to the rainfall concerned

Average values for Frankfurt

Category	Average quantity of rain	Concentration in mg/l				Nos. of cases
		NH ₄	NO ₃	SO ₄	Cl	
I	6,2 mm	4.5	4.9	23.0	5.6	18
II	5,5 mm	2.0	2.4	10.5	2.8	40

The same evaluation was made for the Taunus observatory. Since on that station the average quantity of rain of the cases in group I and II showed great differences (6.8 mms. in group I and 12.1 mms. in group II) we have related the values of concentration of trace-substances of both groups to the average quantity of all cases which is 9.8 mm. With this transformation we receive

Average values for Taunus observatory

Category	Average quantity of rain	Concentration in mg/l				Nos. of cases
		NH ₄	NO ₃	SO ₄	Cl	
I	9,8 mm	2.4	2.9	6.5	1.6	11
II	9,8 mm	1.3	1.8	4.7	1.0	27

We see that the concentration of trace-substances in rain is considerably higher when the rainfall occurred after a period of dry days and the rain-

water is much more dilute when the dry spell between two cases of rainfall was 12 hours or less. We also note that the difference is greater in Frankfurt than on the Taunus. The increased concentration after extended dry periods is caused by the following facts:

- 1) Accumulation of contaminants in the ground layer of the atmosphere during the dry period,
- 2) High number of condensation nuclei at the level of the cloud-base leading to the formation of many small cloud elements,
- 3) Low relative humidity in the cloud-free zone below the cloud base leading to partial evaporation of the drops during their fall through the cloud-free zone and increasing the concentration of trace-substances in the drops by this.

Comparison of the concentration of trace-substances in rain and snow

In our Annual Report No 1, July 1960 we have compared the results of the analysis of 11 cases of snowfall and 38 cases of precipitation from the period November 1956 to May 1957. A similar investigation was carried out from November 1961 to February 1962. 11 cases of precipitation were compared with 11 cases of snowfall. The results are shown in Fig. 9. Column a represents the average concentration of trace-substances in snow, column b the average concentration in rainwater. Since the quantity of rainwater of the 11 snowfalls (average 2.8 mm) is lower than that of the rainfalls (average 6.7 mm) the concentration of trace-substances in rain was transformed to one belonging to a quantity of rain of 2.8 mms (applying the relation: concentration = const. x amount of precipitation^{-0.3}; see next chapter). With this transformation the concentration of trace-substances in rain becomes somewhat higher as can be taken from column c. It is clearly shown that the concentration of trace-substances in snow is nearly twice the concentration of trace-substances in rain, in the case of SO₄ even three times higher than in rain. Only Ca does not show a great difference.

Judging the "surplus" of trace-substances in snow we have to consider the following facts: Within the clouds the incorporation of trace-substances into the cloud-elements will occur in the same way in all cases discussed here since during winter we have snow-flakes within the cloud, whether the precipitation reaches the ground in the form of snow or rain. Freezing-level is low and often below the cloud base during winter-months. The higher concentration of trace-substances in snow flakes as shown in Fig. 9 is therefore caused by pick-up below the cloud base. Snow flakes float through the air and have a longer residence time in the ground layer of the atmosphere. Owing to their large surface they fall very slowly and their fall-velocity does not increase with increasing size. By floating through the air snow flakes sweep a larger volume of air than the straight falling raindrops. The great difference in SO_4 -concentration is a further proof for the high collection-efficiency of snow-flakes and is an indication of the accumulation of sulfate-compounds in the polluted atmosphere near the ground. We believe that the high SO_4 -concentration in snow is not only caused by pick up of particles but also by adsorption of SO_2 followed^{by}/catalytic oxidation.

Relation between the quantity of rainfall and the concentration of chemical constituents in precipitation

It is known from the research of different investigators that the concentration of trace-substances in rainwater is related to the amount of rain. This relation was established by Angström & Högberg (17) as early as 1952. Our own analyses of individual rainfalls showed that high concentrations of trace-substances are generally found in rainfalls amounting to less than 2 mms.

There exist however few cases where low concentrations of trace-substances are related to low amounts of rain. In no case high concentrations of trace-substances were found when the amount of rain was high.

For calculating average values of the decrease of the concentration of trace-substances in rain with increasing amount of rainfall we have classi-

fied the quantities of rain into different categories and we have determined the average concentration for each of the groups:

1) Frankfurt/Main

quantity of rain:	below 0.3	0.31-1.0	1.1-3.0	3.1-7	7.1-11.0	11.0
NH ₄ (mg/l)	13.1	5.0	2.6	1.9	1.6	1.9
NO ₃ (mg/l)	9.3	5.8	2.6	2.0	1.7	1.2
SO ₄ (mg/l)	58.5	30.0	19.8	9.4	7.0	5.8
Cl (mg/l)	17.5	7.1	3.4	1.7	1.4	1.3
Nos. of cases	8	22	42	49	20	15

2) Taunus observatory

quantity of rain:	below 1.0	1.1-3.0	3.1-7.0	7.1-11.0	11.1-20	above 20
NH ₄ (mg/l)	2.9	1.9	1.6	2.1	1.3	0.7
NO ₃ (mg/l)	3.5	2.6	1.9	2.8	1.4	0.7
SO ₄ (mg/l)	9.9	7.4	4.0	5.4	4.4	2.8
Cl (mg/l)	2.5	2.1	1.4	2.0	1.6	1.1
Nos. of cases	4	12	17	13	8	8

We have entered these values in a double-logarithmic scale in Figs. 10 and 11. Fig. 10 shows that the values gained at Frankfurt do not obey a power-law. At quantities below 2 mm rain the decrease of the concentration is sharper than at higher quantities of rain. The trend of the curves for the four components analyzed is very similar. All four curves show the change in the slope. In Fig. 10 we have entered also the curves valid for Taunus observatory as a dashed line. At quantities of rain above 5 mms. the Frankfurt-curves converge towards the Taunus-curves, while at low quantities of rain both curves diverge. In Fig. 11 we have entered the Taunus values. It can be seen that the functions describing the relation between concentration of trace-substances in rain and amount of rainfall on the Taunus ridge obey a power-law. This can be expressed in the following form:

$$\text{concentration} = \text{constant} \times \text{amount of precipitation}^{-0.28}$$

with the exponent having the value between -0.25 (in the case of chloride) and -0.33 (in the case of nitrate).

The more rapid decrease of the concentration at low quantities of rain can be explained in the following way: 1) The ground-layer of the atmosphere in the Main-valley is heavily polluted. The pollutants are washed out by the rain falling through this layer of air below the Taunus ridge. The supply of trace-substances originating from pollution-sources is limited, heavy rainfalls are less contaminated by pollution than light rain.

2) Partial evaporation below the cloud-base leads also to an increase of the concentration of trace-substances in rain. Therefore the relative humidity below the cloud-base influences also the concentration of trace-substances in the rain reaching the ground at Frankfurt. The influence of partial evaporation is greater in light rain than in heavy rain.

Both effects lead to a substantial increase of the trace-substance concentration particularly in light rains. The concentration of rainwater collected on the Taunus observatory is determined mainly by rainout in clouds. When we consider only very heavy rain, yielding amounts around 20 mms, we see that the concentration is more or less equal on Taunus and at Frankfurt.

In Fig. 12 we have compared our own results with those gained by different other investigators. The ordinate indicates the concentration of trace-substances in rain in a logarithmic scale in relative units, the abscissa shows the amount of rain in a logarithmic scale. The first five curves - Angström-Högberg in North Sweden, Georgii-Weber in St. Moritz, Switzerland, Junge, theoretical curve, Podzimek in Czechoslovakia and Sugawara in Japan - show the same features, namely increasing negative exponent with increasing amount of rain. These relations were gained from rainfalls in areas with a limited supply of trace-substances the changing slope indicating that the rainwater becomes more and more dilute during heavy rainfall. The same shape of curve applies to Junges theoretical relation which considers only washout and neglects rainout. The next two curves are those gained at Frankfurt and on Taunus observatory discussed above. The curves gained by Hinzpeter, Becker and Reifferscheid (18) and by Peirson, Crooks and Fisher (19) represent relations between the concen-

tration of radioactive particles attached to rain-droplets and the amount of precipitation. The agreement with our results gained on Taunus observatory is remarkably good. The same applies to the relation gained by Gorham (5) in North England. All these observations show a similar trend. Following Junge we can state that this relation is controlled by liquid water content of clouds, supply of liquid water and amount of precipitation with additional influence of evaporation. Dingle and Gatz (20) have recently investigated the scavenging of radioactive fission products from the atmosphere by rain. In their paper they also discuss the relation given above and suggest that this relationship - which they were not able to substantiate - is only valid in a general way for a large number of observations. We fully agree with the statement by Dingle and Gatz that the relation describes only the long-term average but we must consider that in unpolluted areas the time fluctuations of the concentration of natural atmospheric trace-substances are certainly smaller than the fluctuations of the concentration of radioactive fallout. This will explain that the scatter of the individual measurements is not so wide in our case compared with the scatter of the results gained by Dingle and Gatz.

In addition to the results entered in Fig. 12 we have reanalyzed the measurements of precipitation carried out in Hawaii while the investigations of project "shower" took place in 1955. Fig. 13 shows a schematic cross-section through the Mauna Loa-Mauna Kea saddle with the typical position of the orographic cloud according to W.A. Mordy (21). Along the Saddle Road and the Kulani Road leading to the saddle between Mauna Loa and Mauna Kea special rain-gauges were located. Daily samples of rainwater were collected and analyzed along the following lines: 1) Estimation of total salt-contents in rain-water, 2) Determination of ammonia and nitrate in rainwater. The data of individual analyses were published by E. Eriksson (22). From the great number of rain-gauges located along the two roads we have selected four for our analysis. As indicated by downward directed arrows in Fig. 13 these rain-gauges were positioned in 300 mtrs., 600 mtrs., 1000 mtrs., and 2000 mtrs. altitude. Two of these rain-gauges are situated below the orographic cloud (at 300 mtrs. and 600 mtrs.), the rain-gauge at 1000 mtrs. altitude is located at the cloud-base while

the location of the rain-gauges at 2000 mtrs. altitude is during most days within the cloud. Evaluation of the chemical data of daily rainwater samples with respect to a presumed relation between concentration of chemical components and rate of precipitation reveals the following interesting features as shown in Fig. 14. In Fig. 14 we have entered the salt content of rainwater (in mg/ltr) in dependence of the amount of precipitation (in mms), both in logarithmic scale. We find that at 300 mtrs and 600 mtrs altitude there exists a relation between chemical components and amount of precipitation. The curve valid for the station at 600 mtrs shows some accordance with our St. Moritz curve (Fig. 12) and Junges theoretical curve. The other striking phenomenon is the fact that there exists no relation whatsoever between chemical concentration of rainwater and rate of precipitation in 1000 and 2000 mtrs. altitude, that means at those stations located within the orographic cloud resp. at cloud-base. At these two stations the precipitation was collected within the cloud where it was produced and obviously in such cases the salt-concentration of the raindrops is independent of the rate of precipitation. The salt-concentration of the raindrops collected within the cloud is determined only by processes effective within the cloud and not by wash-out which is effective below the cloud-base. This result suggests that the processes effective below the cloud-base, namely 1) wash-out, 2) additional absorption of trace-gases by droplets and 3) partial evaporation of falling droplets differentiate the salt-content of rain-drops with respect to the amount of rain.

Measurements of the chemical composition of individual rainfalls on the summit of Mt. Zugspitze at 3000 mtrs. altitude in the German Alps reveal the same phenomena. These investigations were performed with the kind assistance of the personnel of the German Weather Service located on the summit which we acknowledge with thanks. From 1 April 1961 to 31 March 1962 156 samples of individual rainfalls were collected on the Zugspitze and analyzed in our laboratory. Some of the analyzed components are entered in Fig. 15. The NH_4 -concentration of Zugspitz-rain as well as the electrolytical conductivity (expressed in microsiemens/cm) do not show any relationship to the quantity of rainfall. Similar as is the case in

~~Hawaii above 1000 mtrs. also on Mt. Zugspitze the summit is in nearly all~~
cases within clouds when it rains. It may be mentioned that the electro-lytical conductivity of Zugspitze-rain is sometimes lower than that of distilled water. Summarizing our results we can generally distinct four types of relationships between the concentration of trace-substances in rainwater and the amount of precipitation. We have compiled these results in Fig. 16.

Type I was found in Frankfurt/M. in the heavily polluted ground layer of the atmosphere. We find a stronger decrease of the concentration at a rate of precipitation below 1 mm. Obviously this is due to the wash-out of the trace-substances accumulated in the polluted ground-layer.

Type II is valid for our measurements on the Taunus observatory, Mt. Kleiner Feldberg at 800 mtrs. altitude and situated above the polluted ground-layer of the atmosphere. In this case the trace-substance concentration of the 700 mtrs. thick ground-layer of the atmosphere between Frankfurt/M. and the Taunus ridge does not influence the result. The same relationship was also found for the concentration of radioactive fission-products in rain averaged from seven German stations, for the radioactivity of rain at Milford Haven and at Bedford/Mass. as well as for the concentration of trace-substances in rain in Northern England.

Type III applies to locations with only little pollution and therefore negligible supply of trace-substances from the ground. We found this relationship to be valid for Ultuna/Sweden, St. Moritz/Switzerland, Hawaii (below the orographic cloud)(Czechoslovakia and Japan), the same shape of curve results also from theoretical considerations by C. Junge (23). In these cases the trace-substance content of the atmosphere is rapidly reduced with increasing quantity of rainfall and a quantity exceeding 5 to 10 mms. leads only to a further dilution of the rain which fell during the first phase.

~~Type IV~~ ~~OR stations situated above the cloud-base there does not exist~~
any relationship between concentration of trace-substances in rain and rate of rainfall. This result was gained on summit of Mt. Zugspitze (3000 mtrs. altitude) and on the slope of Mauna Kea on Hawaii (2000 mtrs. altitude) within the orographic cloud.

The investigation described in this chapter shows the influence of location, altitude, supply of trace-substances and quantity of precipitation for the accumulation of trace-substances in rainwater. Type IV suggests that within clouds the majority of drops has more or less the same trace-substance concentration irrespective of the size of drops.

Detailed differential analysis of individual rainfalls

So far we have dealt with the chemical composition of individual rainfalls considering the total amount of rainwater collected during each case of rainfall. In the further course of our investigation we have studied the behaviour of different chemical constituents in rainwater during the course of individual rainfalls. Our previous study has revealed that the mechanism leading to the removal of trace-substances from the atmosphere and by this action to the accumulation of chemical traces in cloud- and raindrops is very complex and that it is difficult to separate the different processes interfering with each other. A more differential analysis seems therefore desirable and valuable.

Measurements of different chemical components in rainwater were carried out during individual cases of rainfall. Simultaneously the number of large nuclei and Aitken-nuclei was continuously recorded applying an automatic Verzar-counter for the Aitken-nuclei and an automatic impactor for the large resp. the giant nuclei. Fig. 17 shows a typical example of an up-slide rain taking place between 13 and 18 hrs. on 25 Feb. 1960. Measurements of SO_4 -concentration and NH_4 -concentration of rainwater during the rain show a sharp decrease shortly after the onset of rain reaching a minimum of the concentration at about 15 hrs. followed by an increase of the concentration towards the end of rain. Comparing this result with the intensity of rainfall it can be noticed that the 15 hrs.

~~minimum is connected with the maximum of rain intensity, while the increase~~
of concentration at the end of rain (after 17 hrs.) is related to a sharp drop of rain intensity. The continuous production and supply of trace-substances leads to an increase of the concentration of chemical traces in rain when the rate of rainfall is low. With regard to the number of large and Aitken-nuclei measured near the ground during rain our results show that their concentration is only influenced by heavy rainfall. The Aitken-nuclei number drops from about 80000 ccm to 65000/cm at the time of the peak rain-intensity. In a later chapter of this report more information on the relation between concentration of trace-substances in rain and rain-intensity will be presented.

In order to investigate the influence of rain-intensity on the concentration of Aitken-nuclei in the atmosphere at Frankfurt/Main more thoroughly we have evaluated the records of the automatic Aitken-nucleus counter. Fig. 18 shows the relation between Aitken-nucleus concentration and rain-intensity. The numbers in brackets indicate the number of cases. While the average concentration of 996 cases without rain was 68000/ccm the number of Aitken-nuclei in the atmosphere at Frankfurt/M drops constantly with increasing rain-intensity, reaching a concentration of 57000/cm at a rain-intensity of 2.5 mm/hr. This result: reduction of Aitken-nuclei concentration with increasing rain-intensity does not seem to be contradictory to the above stated result: decrease of trace-substance concentration in rain with increasing rain-intensity since the total mass of Aitken-nuclei is too small to account for a substantial increase of trace substance and the effect of wash-out too insignificant that attachment of Aitken-nuclei to rain-drops can account for a detectable influence on the accumulation of trace-substances in rain-water. A relation between the Cl-concentration in rainwater and the intensity of rain (decreasing Cl-concentration in rain with increasing rain-intensity) was also found by A.H. Woodcock and D.C. Blanchard for Hawaii-rains (24). Interesting information on the fluctuation of trace-substance concentration in rain-water during the course of precipitation was also contributed by W. Jacobi (25). Jacobi developed a continuous method for direct measurements of short-lived β -activity in rain. Simultaneous records of β - and γ -

radiation in air near ground-level and of β - and γ -activity in rain indicate maximum values of activity at low precipitation rates. With the beginning of the rainfall the specific activity in air shows a remarkable decrease which is not caused by decrease of Rn-exhalation or air mass change. According to Jacobis assumption the wash-out at ground level indicates the importance of diffusion of particles to rain-droplets. He assumes that the diffusion of RaA is responsible for this wash-out. From his preliminary results a wash-out efficiency of RaA-ions of about 10 % of their specific activity in air per mm rainfall can be estimated.

Our own measurements of Aitken nuclei and large nuclei made during rainfall show however that obviously the rainfall and connected with this the particle wash-out is only effective in heavy rain that means at rain-intensities above 1 mm/hr. Only such intense rainfalls may really reduce the ground-level aerosol concentration. In all other cases the quantity of particles washed-out is replaced by the continuous supply of freshly produced aerosols.

Continuous records of the electrolytical conductivity of rainwater

The differential analysis of chemical components in rainwater during rainfall is a very time-consuming and laborous task. On the other hand it is not possible to record many different chemical components continuously during the fall of rain.

As mentioned in an earlier chapter of this report, the electrolytical conductivity of rainwater is an excellent indicator for the total concentration of inorganic ions in rainwater and by this for the total trace-substance concentration. The fluctuations and time-variations of the trace-substance concentration during rainfall can easily be studied by continuous records of the electrolytical conductivity.

The method applied was the following: A collecting funnel with 0.5 m² surface was placed on the roof of the institute's building. The rainwater is led through a polyethylene tube and passed through a cell taking 10 ccm

of water. The platinum electrodes were coated with a thin layer of platinum chloride to prevent polarization. Figs. 19a and 19b show a schematic diagram of the instrumentation used which includes a continuous recording pH-meter, continuous recording conductivity-meter and instrumentation for measuring the total beta-activity of rainwater. In our Annual Report No 2 (August 1961) and in Annual Report No 3 (December 1962) we had published a number of records of the trace-substance concentration in rainfalls.

In the meantime a great number of cases has been recorded showing some characteristic features which we will discuss in the following typical examples.

Fig. 20 shows an individual shower. The electrolytical conductivity, indicating the concentration of trace-substances in rainwater, drops sharply after the beginning of rain. At the same time the intensity of rain increases. On the other hand with the decrease of the rain-intensity towards the end of the shower an increase of the trace-substance concentration in rainwater is connected. Fig. 20 shows a typical example of the inverse relation between intensity of rain and trace-substance concentration which can be found in the majority of showers. It is furthermore of great interest to see that the level of the cloud-base lifts towards the end of the shower. This causes an increase of the cloud-free layer through which the raindrops fall before reaching the ground. When the cloud-base raises the chance for droplet-evaporation increases. Therefore the increase of the electrolytical conductivity towards the end of the shower can very well be caused by the partial evaporation of falling raindrops. This would be in agreement with assumptions by Hosler, Salter and Kruger (26). In the upper part of Fig. 20 we have entered the SO_2 -concentration in the atmosphere during the time of the shower which shows a drop of the concentration while it is raining. Also the wind-distribution has been entered.

Fig. 21 shows the fluctuation of trace-substance concentration during a series of showers. Each shower is connected with the next one by slight rain and at the beginning of each of the showers the concentration shows

a peak. It can however be noticed that the peak-height of consecutive showers (1,2,3,4,5) drops indicating that the supply of trace-substances fed into the clouds is limited. We can deduce from the observations that each shower is produced from its own shower-cell. The main part of trace-substances is incorporated into the cloud-droplets by rainout. When the shower starts the accumulated amount of trace-substances is brought down to the ground by falling raindrops. Except for shower 6 a downward trend of the record of electrolytical conductivity exists. Besides the intensity of rainfall we have also entered the atmospheric SO₂-concentration and the average wind-velocity.

Fig. 22 shows the electrolytical conductivity of a series of showers measured between 11.00 hrs. and 16.00 hrs. on 13 July 1961. During each one of the four showers the electrolytical conductivity drops but it is higher at the beginning of the next consecutive shower compared with the end of the previous one.

This indicates a fresh supply of trace-substances into the clouds during the dry interval between two showers. Besides the measurements of the electrolytical conductivity we have entered some results of analyses of the NO₃-concentration in rainwater. The general trend of the NO₃-variations agrees well with that of the electrolytical conductivity.

In the upper part of Fig. 22 we have plotted the SO₂-concentration of ground-level air during the showers. These records suggest a slight drop of the SO₂-concentration at the time of the maximum of shower-intensity. It can generally be stated that the SO₂-content of the air in the ground-layer of the atmosphere is not much affected by rain.

In the lower part of Fig. 22 we have plotted the net total electrolytical conductivity (and NO₃-concentration) of rainwater independence of the total amount of rain fallen during the four showers. This diagram shows the conductivity of the total sample (resp. the NO₃-concentration of the total sample) $\sum K_i V_i$ against the quantity of rain $\sum V_i$. It can be seen the cumulative conductivity (or NO₃-concentration) K (averaged from

the individual samples collected during the rain) drops with increasing quantity of rain. The samples collected towards the end of the showers consist of water having nearly the same purity as distilled water. Fig. 22 suggests that towards the end of each shower a dilution process takes place diluting the initially high salt content of rainwater fallen at the beginning of the shower. In the time interval between two showers the trace-substance concentration of the atmosphere is regenerated and we can also assume that each shower is generated from individual cloud-cells which would explain the high conductivity at the beginning of each individual shower. Comparison of our data of electrolytical conductivity with those gained by R. Siksna (12) in Sweden and A.K. Mukherjee (27) in India reveals that the electrolytical conductivity of Frankfurt-rains is about twice (compared with Siksna) to five times (compared with Mukherjee) higher being a result of the higher concentration of atmospheric trace-substances in middle Europe.

Fig. 23 shows an example of continuous rain. Again we have entered four different components which were simultaneously recorded - wind-velocity (m/sec), SO_2 -concentration (mg/m^3), rain intensity (mm/hr) and the electrolytical conductivity of rainwater ($\mu\text{mS}/\text{cm}$). This rainfall was connected with the passage of a warmfront. It can be seen that the electrolytical conductivity decreases sharply during the first two hours of rainfall and remains more or less constant during the remaining part of the rain. This is typical for rain connected with slow upslide motions in the atmosphere in contrast to showers in which case the electrolytical conductivity shows much more intense fluctuations.

It is interesting to note that the SO_2 -concentration of the atmosphere shows a similar trend as the concentration of trace-substances in rainwater. During the first two hours of rainfall the SO_2 -concentration drops with heavy fluctuations from approximately $0.6 \text{ mg}/\text{m}^3$ to $0.2 \text{ mg}/\text{m}^3$. After 15.00 hrs. when the intensity of the rain becomes very low and particularly during the dry spell between 16.00 hrs. and 17.00 hrs. the SO_2 -concentration increases again. With the beginning of the rain after 17.00 hrs. another drop of the SO_2 -concentration can be observed which continues

to the end of the rain.

Fig. 24 shows a similar case. The rainfall was connected with the passage of a warmfront. The trend of the electrolytical conductivity is very much like that shown in Fig. 23. More details of these cases of continuous rain connected with upslope motions have been given by Georgii (28) elsewhere.

Summarizing these results of the investigation of trend and fluctuation of the trace-substance concentration in rainwater during the course of individual rainfall we can standardize all cases into three categories 1) showers, 2) series of showers, 3) continuous rain. The behaviour of the electrolytical conductivity of rainwater in relation to the intensity of rainfall is schematically shown in Fig. 25 for these three categories. Individual showers have an inverse relation between rain-intensity and trace-substance concentration in rainwater. During a series of showers we find a general decrease of the trace-substance concentration during the course of the different showers, there are however heavy fluctuations to be observed during each shower and every time the intensity of the shower increases the trace-substance concentration shows also a peak. The fluctuations of the electrolytical conductivity are therefore very intensive. Continuous rain shows a much smoother record. In most cases the trace-substance concentration drops sharply at the beginning of the rain and remains more or less constant during the further course of the rain. Fluctuations of intensity and electrolytical conductivity are small.

Relation between the intensity of rainfall and the concentration of trace-substances in showers

The records of the trace-substance concentration in rainwater gained during showers revealed that in most cases high concentrations are connected with low intensities of rainfall while low concentrations occur during periods of high intensity of rainfall. We have investigated these

relations for a number of cases and entered the results in Fig. 26. The examples entered in this diagram are arranged according to increasing intensity of rain. It can easily be seen that increasing intensity is connected with a decrease of the trace-substance concentration. On the right side of Fig. 26 we have summarized the ten cases and shown the average trend between concentration, plotted as electrolytical conductivity and rain-intensity. This summarizing curve shows that the concentration decreases with increasing intensity according to the following equation:

$$K = \text{const.} \times I^{-0.33}$$

This relation is a first approximation for the relation between rain-intensity in showers and trace-substance concentration. The power-law is not exactly valid since the slope of the curve in the double-logarithmic presentation has a downward trend when higher intensities are concerned. This indicates a deficiency in the supply of additional trace-substances at high intensities of rain. Below this summarizing curve we have entered in Fig. 26 two additional curves comparing our own results with theoretical calculations by Jacobi (29). In his computations Jacobi considered only rainout and the collection of cloud-droplets by falling raindrops. His curves indicate the relation between rain-intensity and concentration of radioactive traces in rainwater. He assumes a constant droplet-size distribution in Stratus respective Cumulus-clouds during the rain and a given concentration of radioactive material in the cloud-droplets. We see that his curve for Cumulus clouds shows quite good agreement with our curve based on observations.

To explain the relation between intensity of rainfall and trace-substance concentration in rainwater, we have to mention the following facts:

As a first approximation we can assume that the number of drops per unit volume be constant and that a change of the intensity of rain is caused by a change of drop size. This could be expressed in the following way:

$$K \sim I^{-a} \quad K \sim r^{-b}$$

The concentration would not only be inversely proportional to the intensity but also to the average size of raindrop. According to our observations the relationship would be

$$K (r^3)^{-0.5} = K r^{-1}$$

This relation shows agreement with results of investigations carried out by Turner (30) who found that the salinity of small drops is higher than that of large drops.

Stierstadt and Kadereit (31) using a raindrop spectrometer of own design investigated the specific activity of rain in dependance of the drop size. In agreement with Turners results they also found - in their case for radioactivity - that the specific activity of raindrops decreases with increasing drop-size. They give the following values:

average diameter of drops	specific activity
0.5 mm	1.0
0.65 mm	0.74
0.9 mm	0.73
1.2 mm	0.61

With respect to the assumptions made, namely that a change of rain-intensity is connected with a change of drop-size, these are supported by investigations carried out by Best (32). He found that the average drop-size increases with increasing rain-intensity according to the empirical equation:

$$r \text{ (mm)} = 0.53 \times I^{0.199} \text{ (mm/hr)}$$

Grunow (33) investigated fluctuations of the rain-intensity in relation to the change of the average drop-size and to the change of the drop-number per unit volume. He found that in the case of continuous rain connected with upslide-motions the variations of the intensity are proportional to the drop-size while the number of drops changes only slightly. In the case of showers variations of the rain-intensity are connected with changes of the average drop-size as well as with changes of the number of drops. Finally, in the case of showers connected with the passage of cold-fronts variations of the rain-intensity are mainly related to variations of the number of drops. The results of Grunows investigations present a rather complex picture of these variations in the structure of precipitation which obviously require a more detailed study.

The budget of trace-substances in precipitation

From 1960 to 1962 chemical analyses of cloud-water as well as rainwater were carried out at three stations in different altitudes, namely Frankfurt/Main, Taunus observatory, Kleiner Feldberg (800 mtrs. altitude) and Zugspitze (2960 mtrs. altitude). During the course of these investigations the summit of the Zugspitze was frequently within clouds, the Taunus observatory, when in clouds, was mostly very near the cloud base while our station at Frankfurt was below the cloud-base in the majority of cases.

For the sampling of cloud-water a device as illustrated in Annual Rep. No 3 was used. Under a cover to prevent intrusion of rain a cylindrical plastic wire-mesh collects the cloud-drops from the air-volume passing the mesh. The fog collector is mounted on a normal rain-gauge. Instruments of this type have been successfully used by Grunow (34).

A summary of the results of chemical analyses in non-precipitating and in precipitating clouds shows Fig. 27. Here we have entered the average values of the electrolytical conductivity of cloud- and rainwater collected at the three different sampling-stations. The electrolytical conductivity represents a true picture of the total concentration of soluble inorganic components in the samples.

With regard to budget-considerations we will discuss non-precipitating clouds at first: As can be seen in Fig. 27 the concentration of trace-substances in cloud-water is very high near the cloud-base. The high values of electrolytical conductivity near the cloud-base can be explained by 1), the supply of trace-substances from the ground carried upwards and collected by the cloud-droplets near the condensation-level, and 2) by the low liquid-water content of the cloud near the cloud-base.

Within the cloud we find with increasing altitude a decrease of the electrolytical conductivity of cloud-water. In 3000 mtrs. altitude the concentration of the cloud-water amounts to only approximately 15 % of the values found in 800 mtrs. altitude. This dilution can be explained 1) by the lack of additional supply of trace-substances with increasing

altitude and 2) by the increasing liquid water content of the cloud set free by condensation with increasing altitude.

With respect to precipitating clouds we receive the following picture: The concentration of trace-substances in rainwater in 3000 mtrs. altitude is of the same order of magnitude as in cloud-water. This is to be expected since the formation of precipitation-elements takes place in higher levels of the cloud. During the fall of the precipitation-elements through the cloud their concentration with respect to chemical components does not increase furthermore. The electrolytical conductivity of rain in 800 mtrs. altitude is not higher than in 3000 mtrs. provided that the lower sampling-station is within the precipitating-cloud.

Only during the fall of the precipitation-elements through the cloud-free zone below the cloud-base we observe an increase of the chemical concentration of rain-water due to "wash-out" as well as by partial evaporation of the rain-drops during their fall through the unsaturated air. This increase of the concentration of trace-substances which can be attributed to wash-out as well as evaporation amounts from 20 % to 40 % of the total concentration of trace-substances in rain-water at ground-level.

The survey given above and demonstrated in the schematic diagram of Fig. 27 permits the conclusion that on the average approximately $\frac{2}{3}$ of the trace-substance concentration found in rain-water at ground-level has been incorporated within the clouds and $\frac{1}{3}$ can be attributed to processes taking place below the cloud-base.

This ratio fluctuates of course from case to case. The evaluation of 94 cases of precipitation on the Zugspitze resp. 70 on Kl. Feldberg/Taunus during 1961/62 and of 27 analyses of cloud-water samples on Zugspitze resp. 40 samples on Kl. Feldberg/Taunus during the same period show that the ratio of "rain-out" (incorporation within clouds) to "wash-out" (impaction below the cloud-base) depends strongly on the amount of rainfall. When the amount of rainfall does not exceed 1 mm, the contribution of "wash-out" and evaporation to the total concentration

of trace-substances may amount to 60 %, while it may drop below 20 % when the amount of rainfall exceeds 5 mm.

The ratio of the concentration of trace-substances in precipitation to the concentration in cloud-water varies also with respect to the different chemical components. The data presented in the survey in Fig. 27 lack under the condition that the three sampling stations are separated by a large horizontal distance. During summer 1963 we were able to organize four sampling stations for cloud- and rainwater near Innsbruck-Austria. We are grateful to Professor Hoinkes, department of Meteorology and Geophysics, University of Innsbruck and his colleagues for the cooperation extended to us.

These sampling stations are separated by a vertical distance of 1800 mtrs. and a horizontal distance of only 6.5 kms. Fig. 28 shows a vertical profile of the four stations. Under these provisions we are certain that the rain falling at these four sampling stations originates from the same precipitation-process, that means from the same cloud-system. Apart from that, the two stations in 1800 mtrs. altitude and in 2300 mtrs. altitude are inside the clouds, when it rains. We can therefore distinguish between the incorporation of trace-substances into rain-elements by rainout and by washout.

During summer 1963 we have analyzed ten cases of rainfall which were collected during simultaneous rainfalls at the four stations. In Fig. 29 we have plotted the results. It can be seen that the amount of rainfall which was recorded at Innsbruck - base-station was only about 70 % of that recorded at the same time on Hafelekar. The amount of rain on Hafelekar was normalized to 100 %. This increase of the quantity of rain with increasing altitude is a well-known fact to meteorologists. The electrolytical conductivity representing the total-trace-substance concentration in rainwater on Hafelekar is 63 μ when we normalize the Innsbruck-value to 100 %. This is in agreement with the data given in the survey in Fig. 27 showing that about 2/3 of the total trace-substance concentration measured at the ground had been incorporated inside the

clouds, mainly by rainout while about $1/3$ of the total trace-substances have been incorporated below the cloud-base and are a result of washout and partial evaporation.

With respect to the individual ions analyzed, Fig. 29 shows a considerable difference with respect to the decrease of concentration with altitude. While the Na-concentration decreases quite strongly and was found to be only 20 % on Hafelekar compared with the Innsbruck-value the concentration of Chloride in rainwater is 80 % on Hafelekar compared with the Innsbruck-value..

Conclusions

The chemical analysis of individual rainfalls reveals a decrease of the concentration of trace-substances with increasing quantity of rainfall. Four different types of the relationship can be established. The validity of each type depends on the location of the sampling station and the supply of atmospheric trace-substances into the raining clouds. Investigations on mountain tops inside clouds show that this type of relation does not hold for rain collected within clouds. This stresses the importance of the processes taking place below the cloud-base (washout and evaporation) for establishing the relation between concentration of trace-substances and quantity of rain.

Analysis of the trace-substance concentration in rain and snow carried out simultaneously during the winter-period emphasise the high collection efficiency of snow-flakes below the cloud-base.

Detailed analysis of chemical components in rainwater during the course of individual rainfalls and continuous records of the electrolytical conductivity show that variations of the trace-substance concentration of rainwater are influenced by changes of rain-intensity and by changes of the altitude of the cloud-base.

Investigations carried out at stations in different altitudes present information on the relative importance of rainout and washout. Approximately 50 % to 80 % of the total concentration of trace-substances measured at the ground are incorporated inside the clouds. The exact ratio rainout/washout depends very much on the quantity of rain fallen during each individual case of precipitation.

Besides aerosol-particles soluble gas-traces are incorporated into cloud- and raindrops. Estimations on the importance of gas absorption for precipitation chemistry indicate that this process may contribute considerably to the total trace-substance concentration in rainwater. This has been demonstrated by preliminary experiments. These investigations aiming to determine the collection efficiency of droplets for gas traces will be continued with an instrumental setup representing more closely atmospheric conditions. It will also be necessary to conduct more research on the partial evaporation of drops during their fall through the cloud-free layer below the cloud-base.

The authors gratefully acknowledge the assistance given by the personnel of the German weather service on Zugspitz-observatory, by Professor Hoinkes and Miss I. Lauffer of the Department of Meteorology and Geophysics, University of Innsbruck, by Dr. Stierstadt of the Department of Physics, University of Munich and by the scientific and technical personnel of the Department of Meteorology and Geophysics, University of Frankfurt.

Spurenstoffverteilung in der Atmosphäre

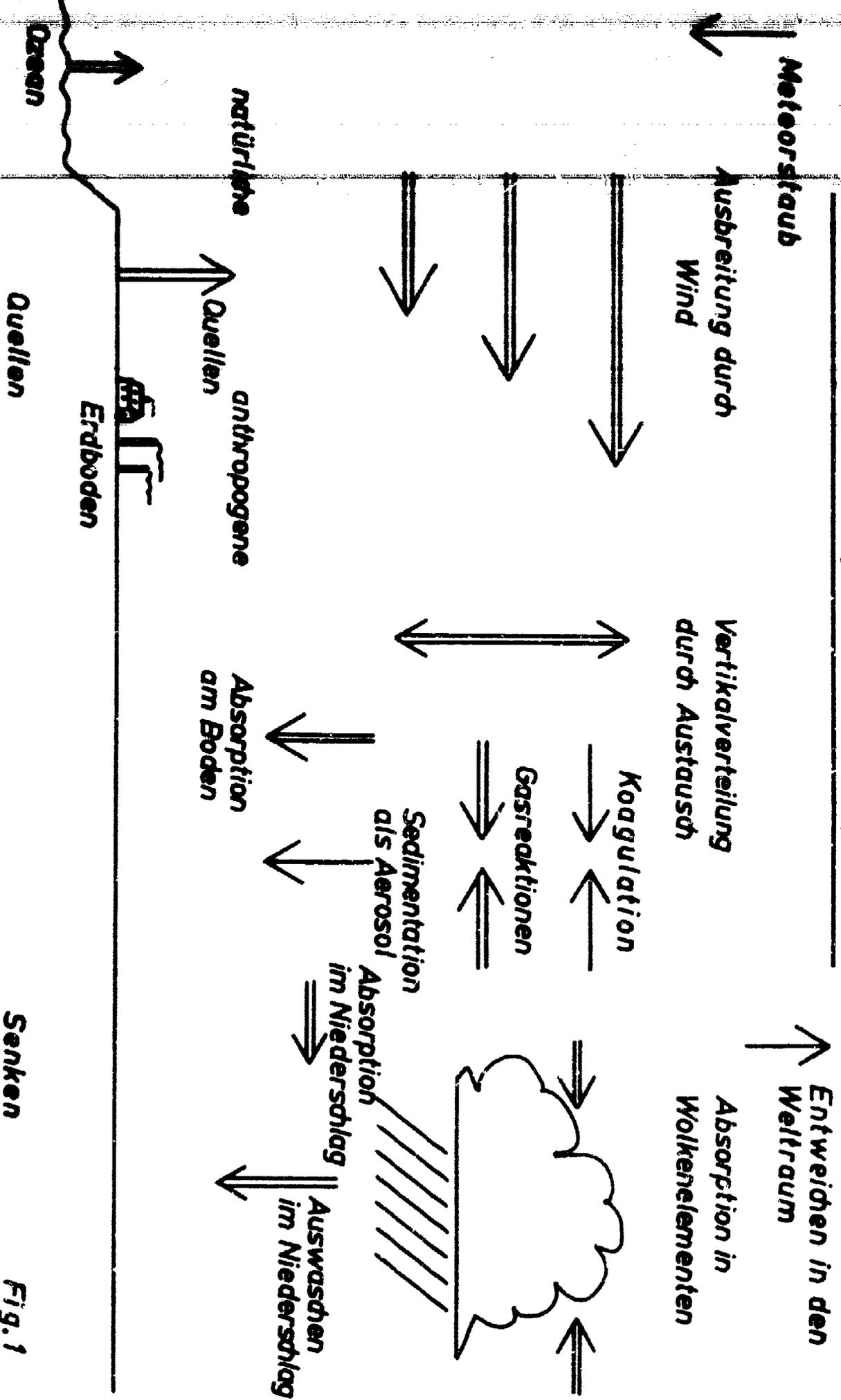


Fig. 1

Aerosole

Spurengase

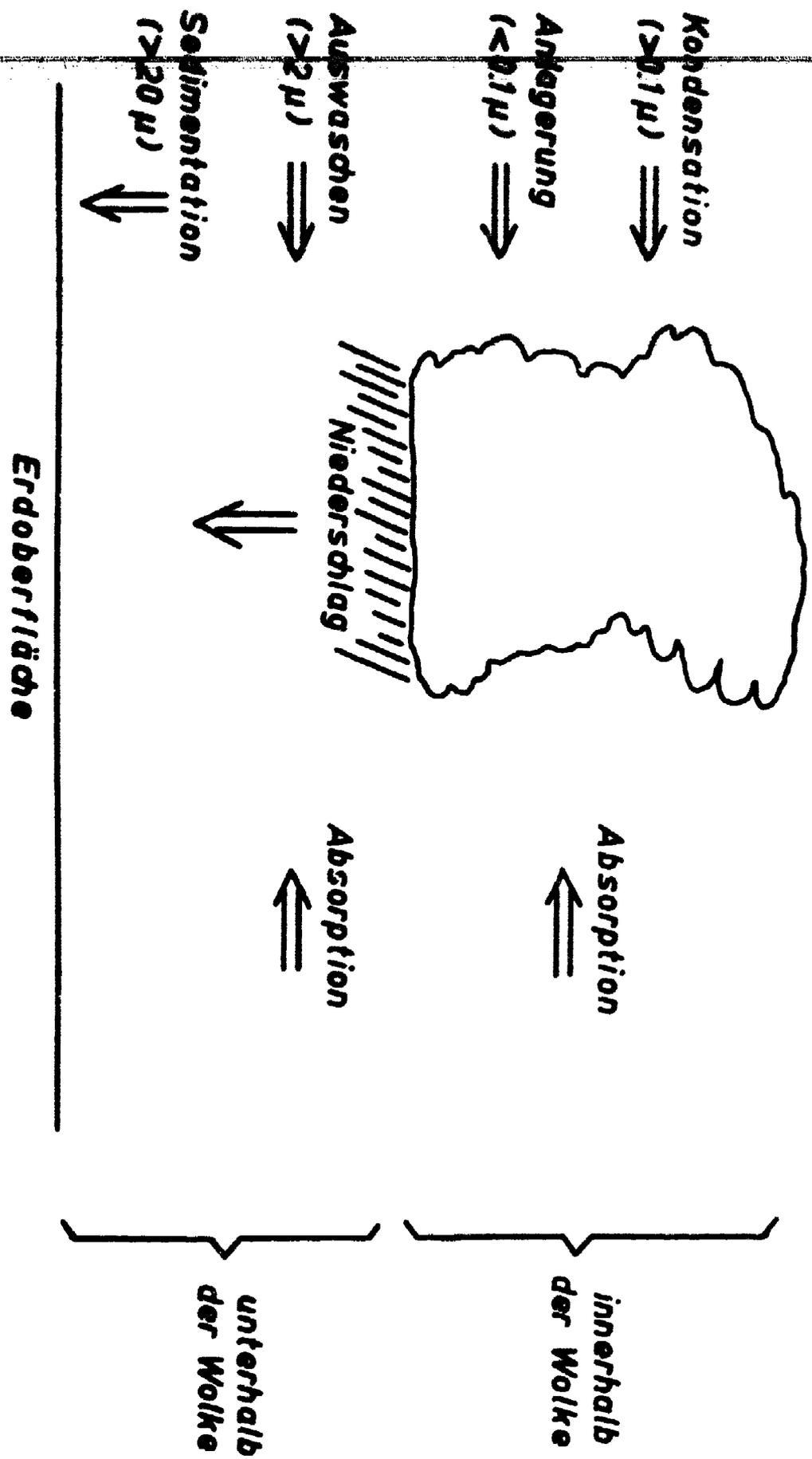
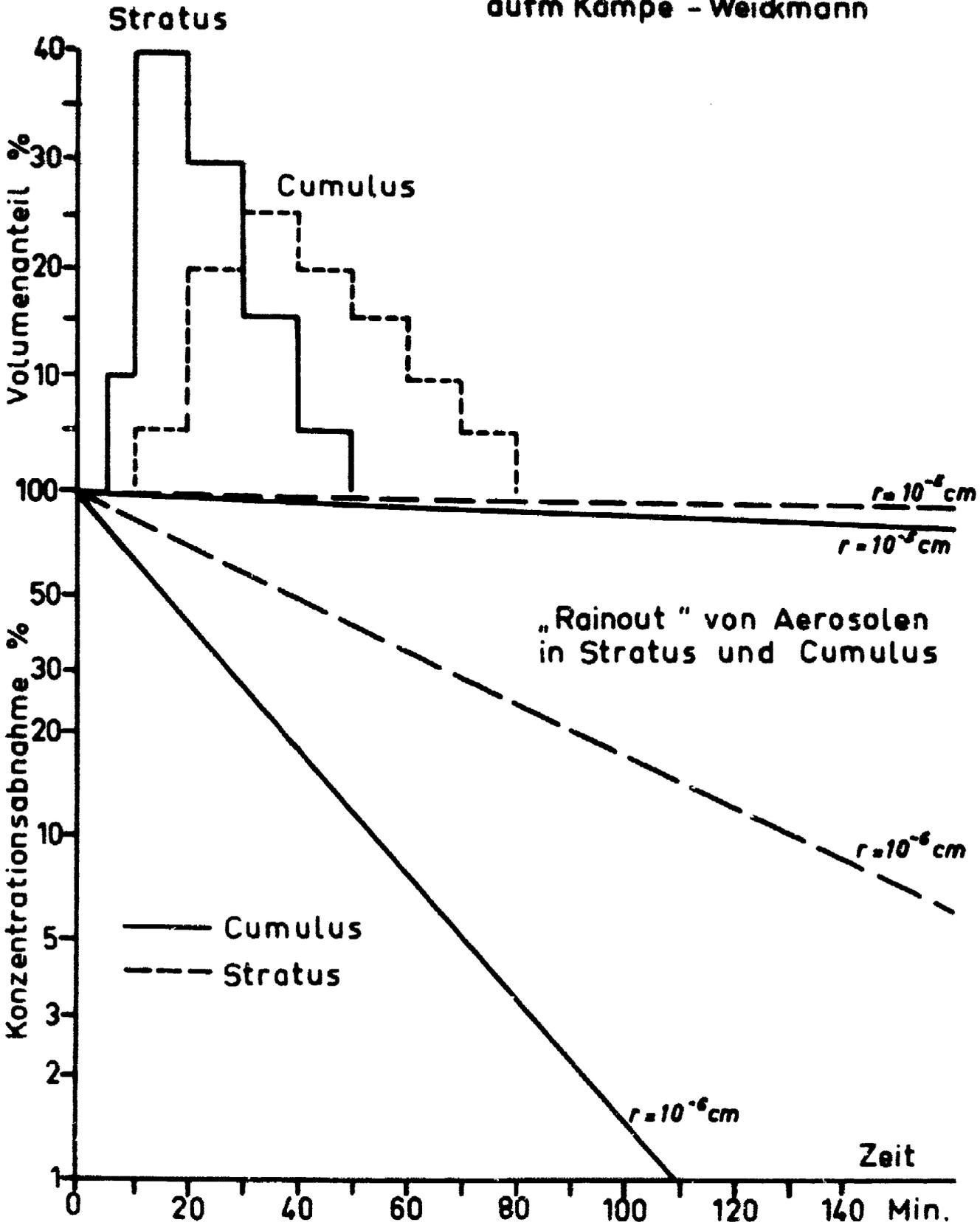


Fig. 2

0 10 20 30 40 50 μ Tropfenradius

Tropfengrößenverteilung der Wolken-
elemente in Stratus und Cumulus
nach Houghton
aufm Kampe - Weickmann



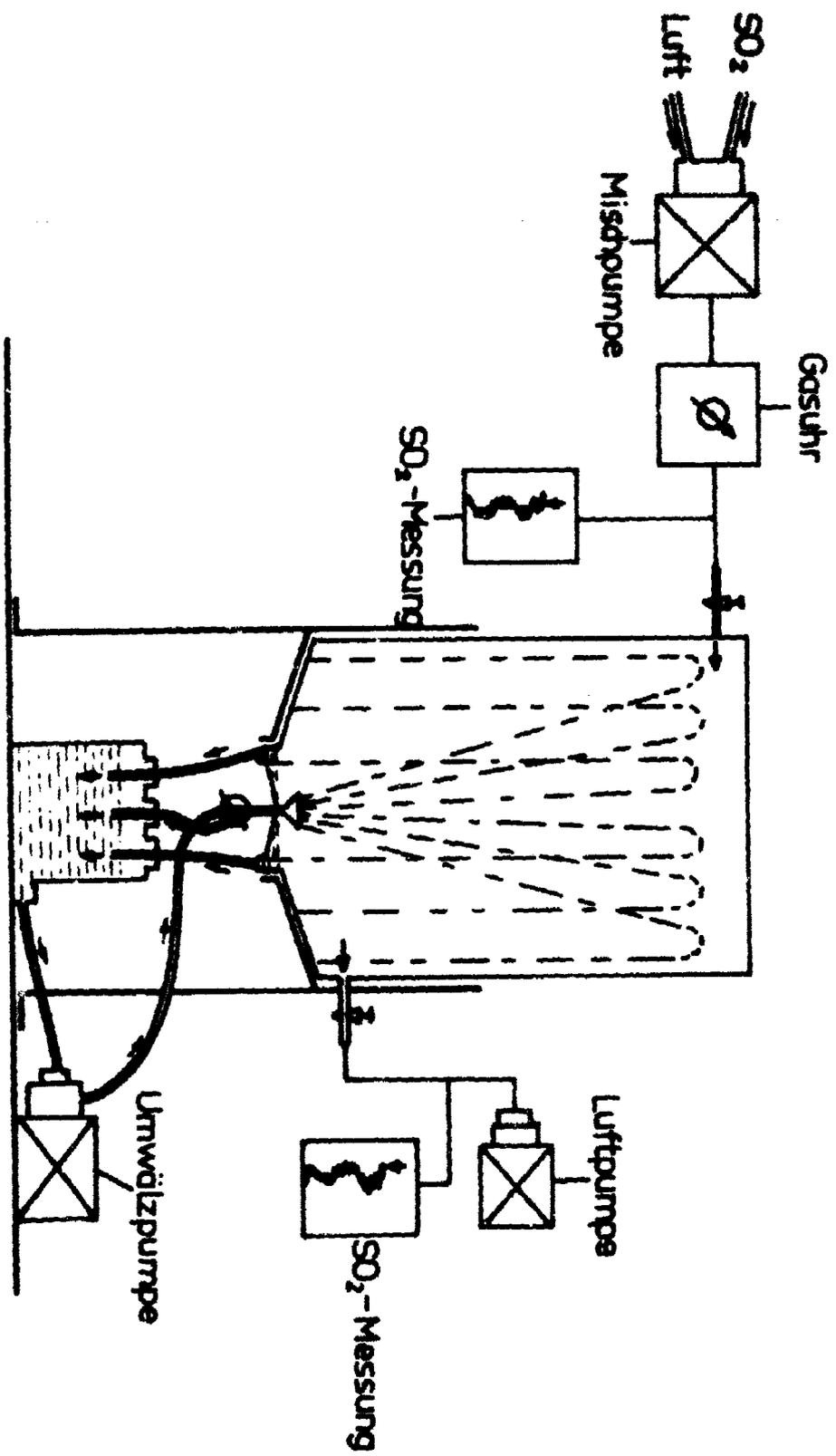
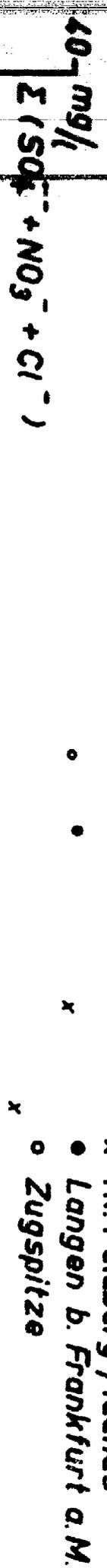
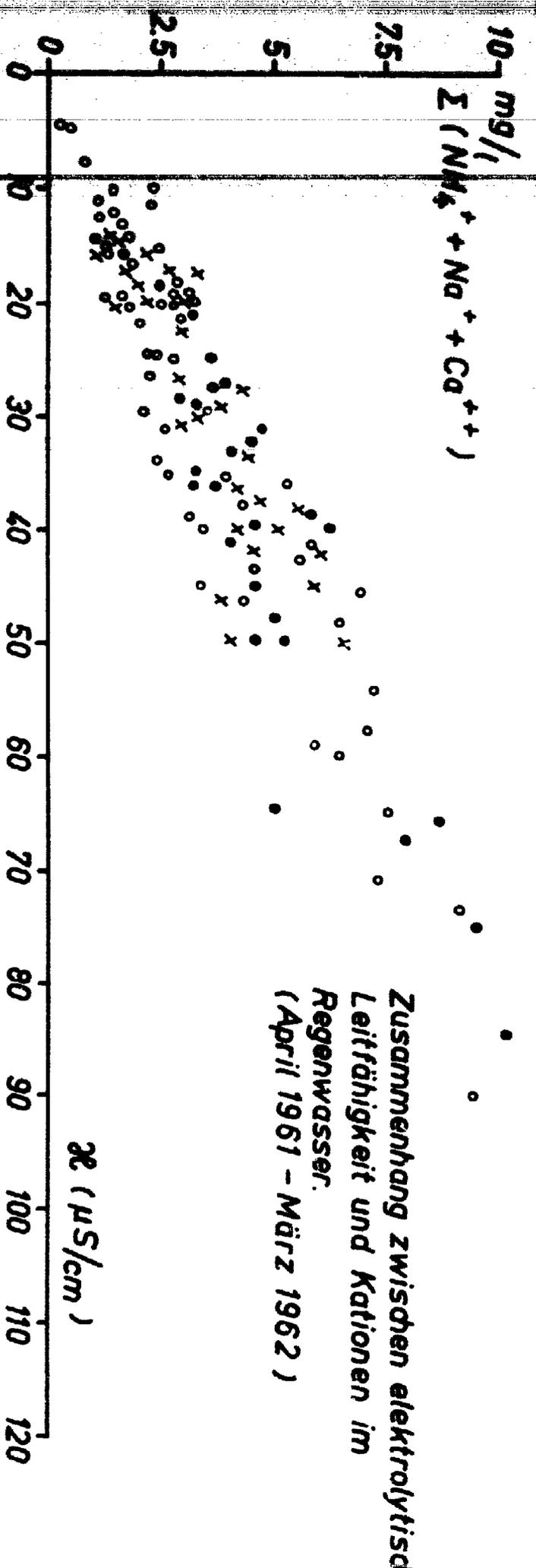


Fig. 4



x Kl. Feldberg / Taunus
 • Langen b. Frankfurt a.M.
 o Zugspitze

Fig. 5

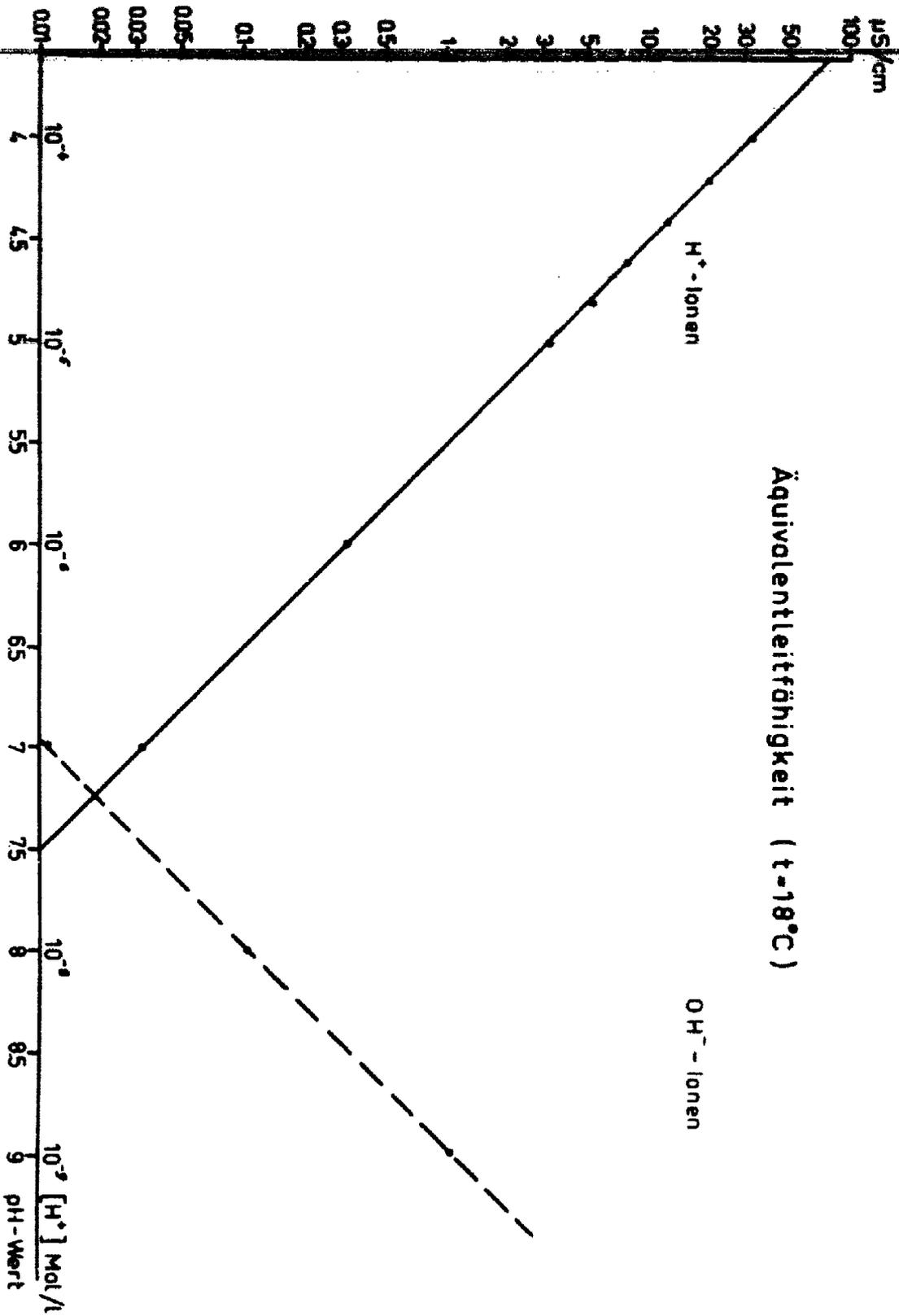
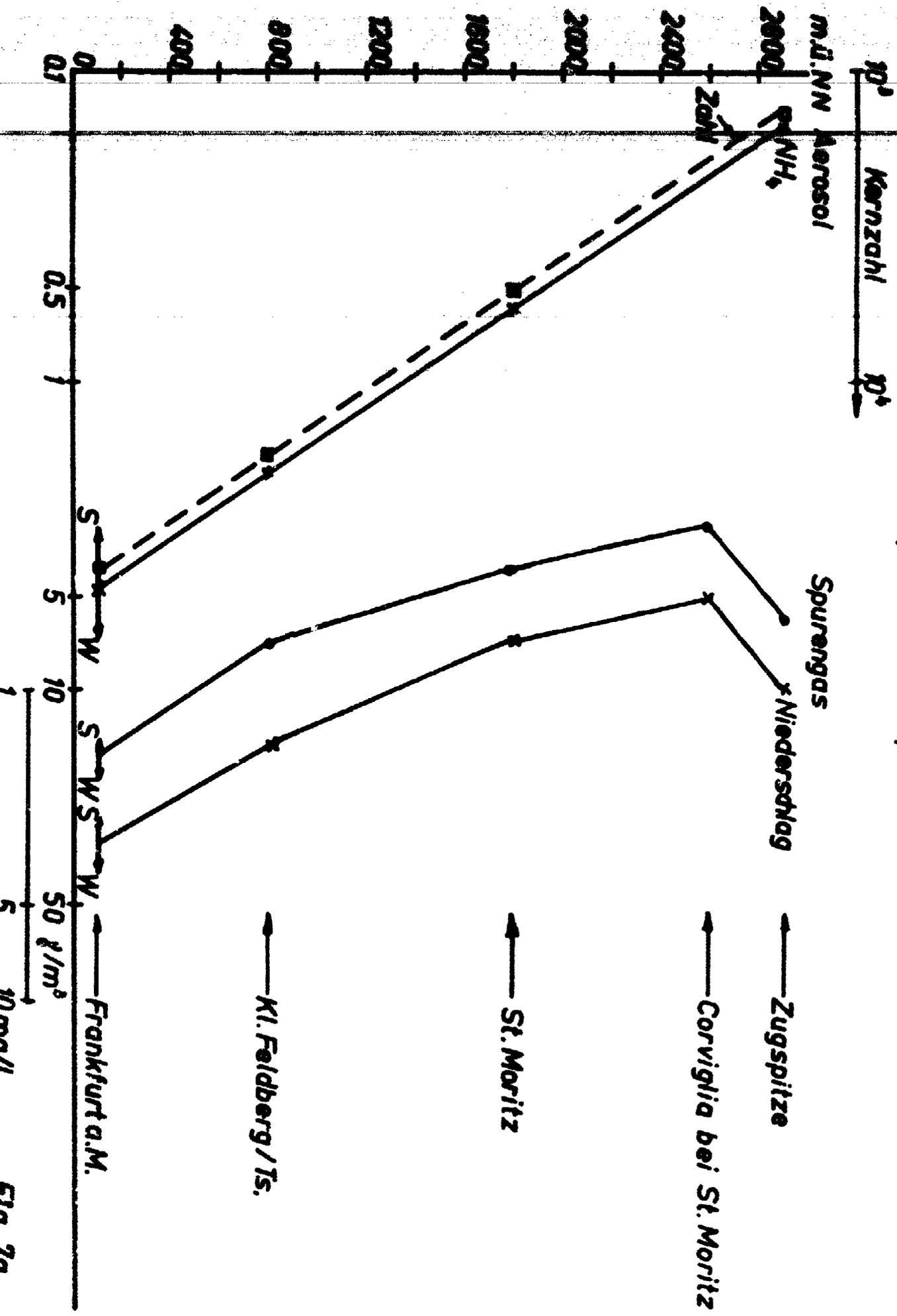


Fig. 6

Verteilung von NH_4 in Gasphase, flüssiger u. fester Phase



Verteilung der NO₂-Konzentration in Gasphase, flüssiger u. fester Phase

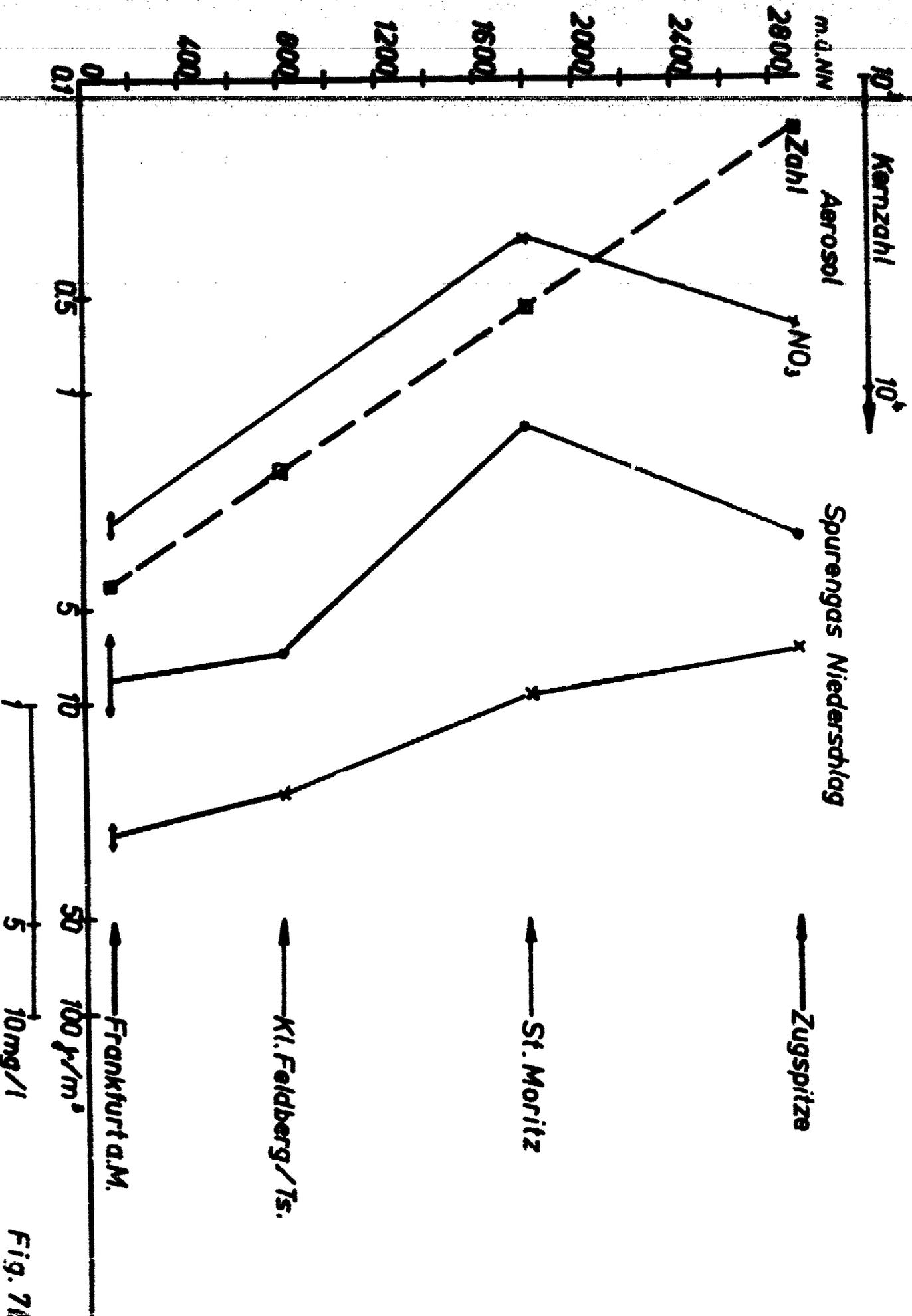
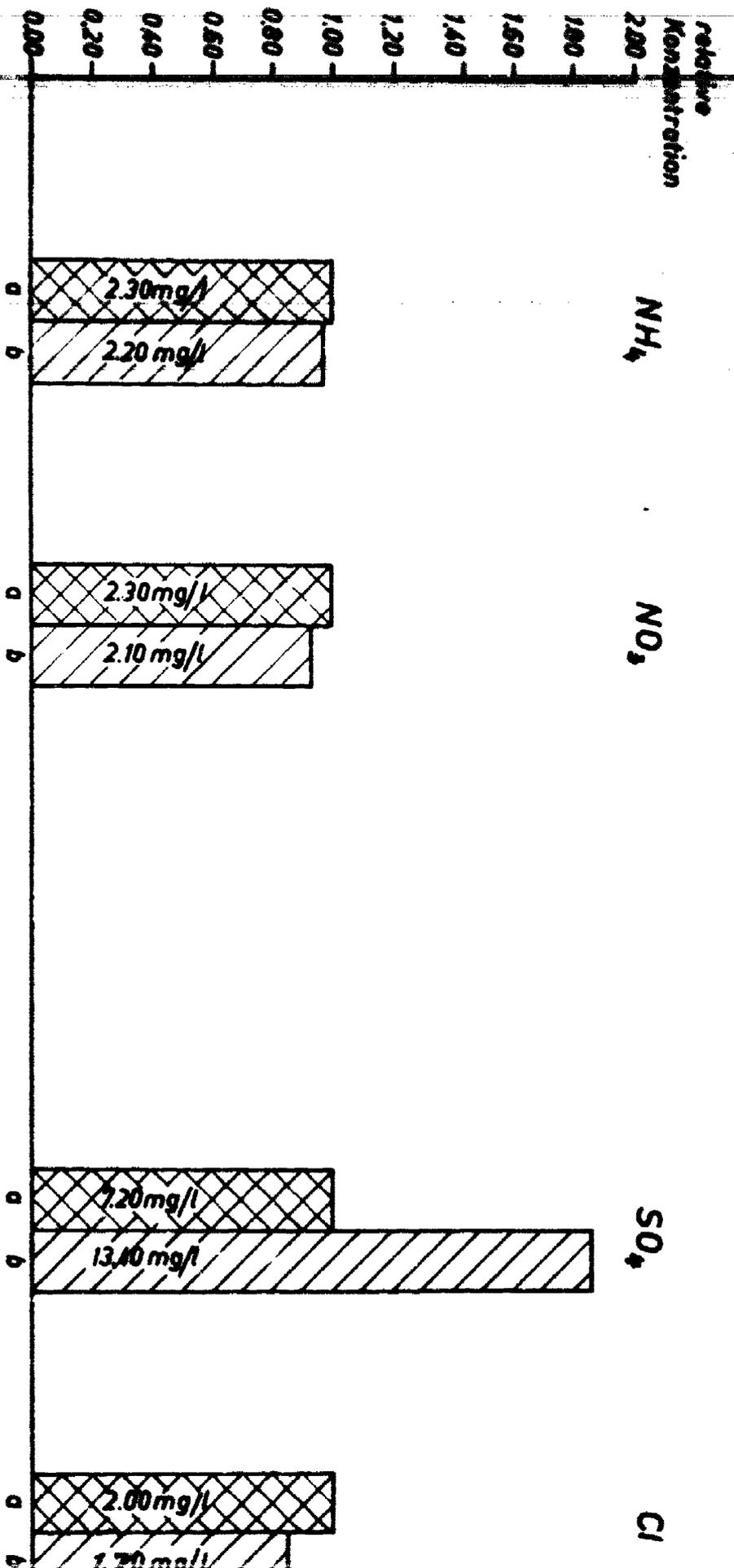


Fig. 7A

Verhältnis der Spurenstoffkonzentration in Schauern und Landregen in Frankfurt a.M.

Juli 1956 - Dez. 1957

a - Schauer (21 Fälle)
 b - Landregen (44 Fälle)
 } nur Regenfälle > 2,0 mm



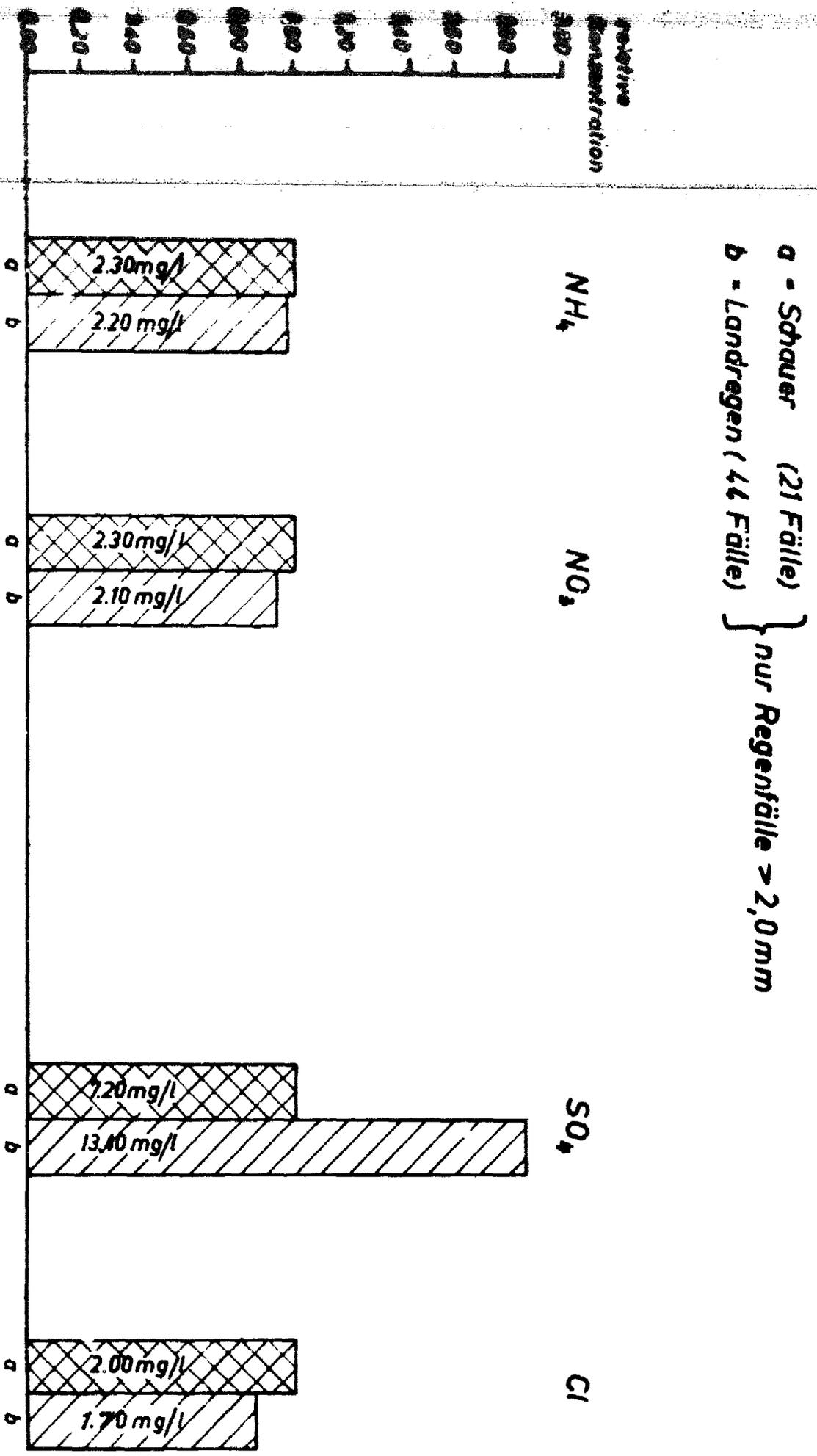


Fig. 8

Frankfurt a.M. Juli 1956 — Dez. 1957

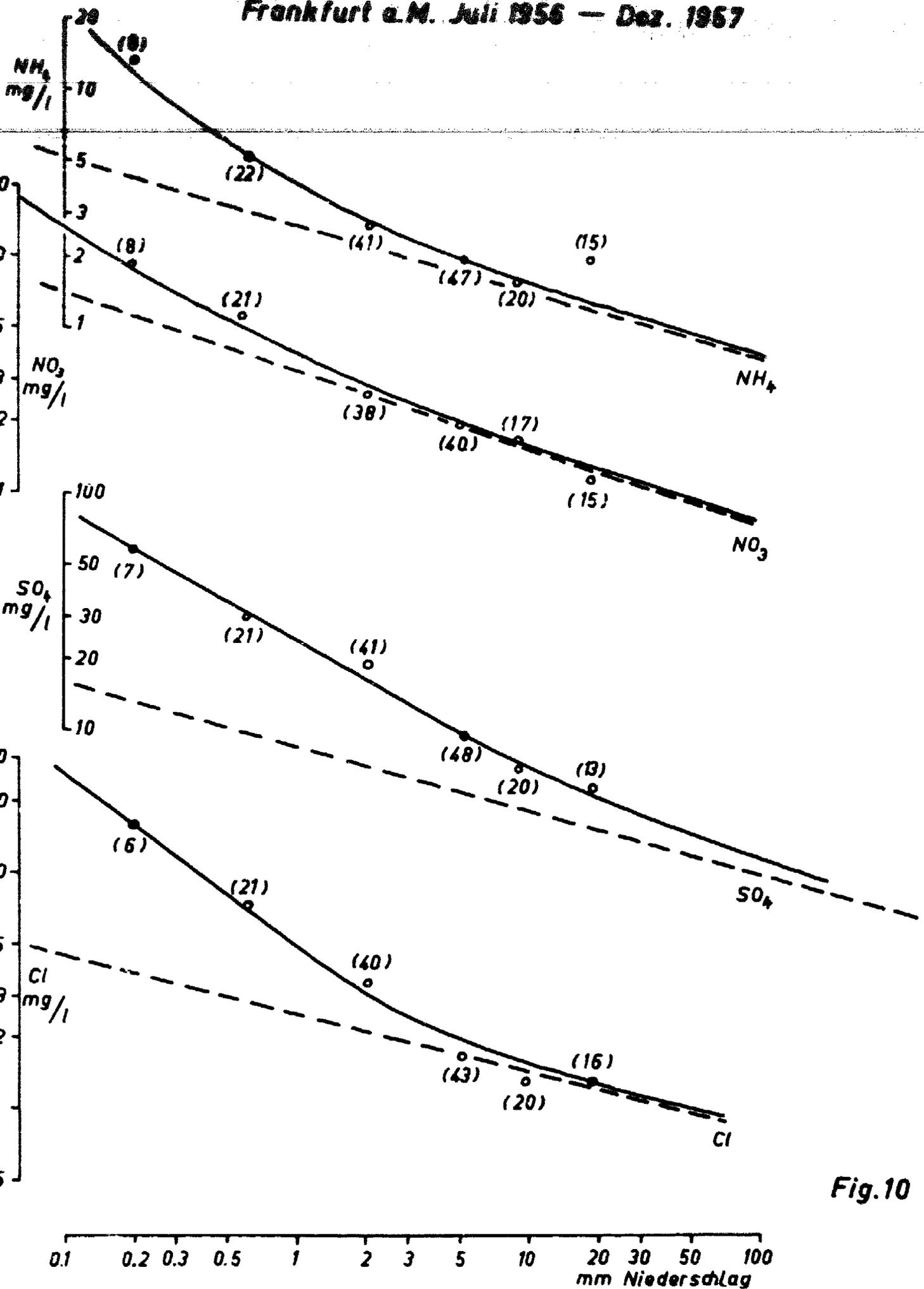


Fig.10

**Chemische Analyse
von Einzelniederschlägen
Kl. Feldberg/ Ts. März — Dez. 1957**

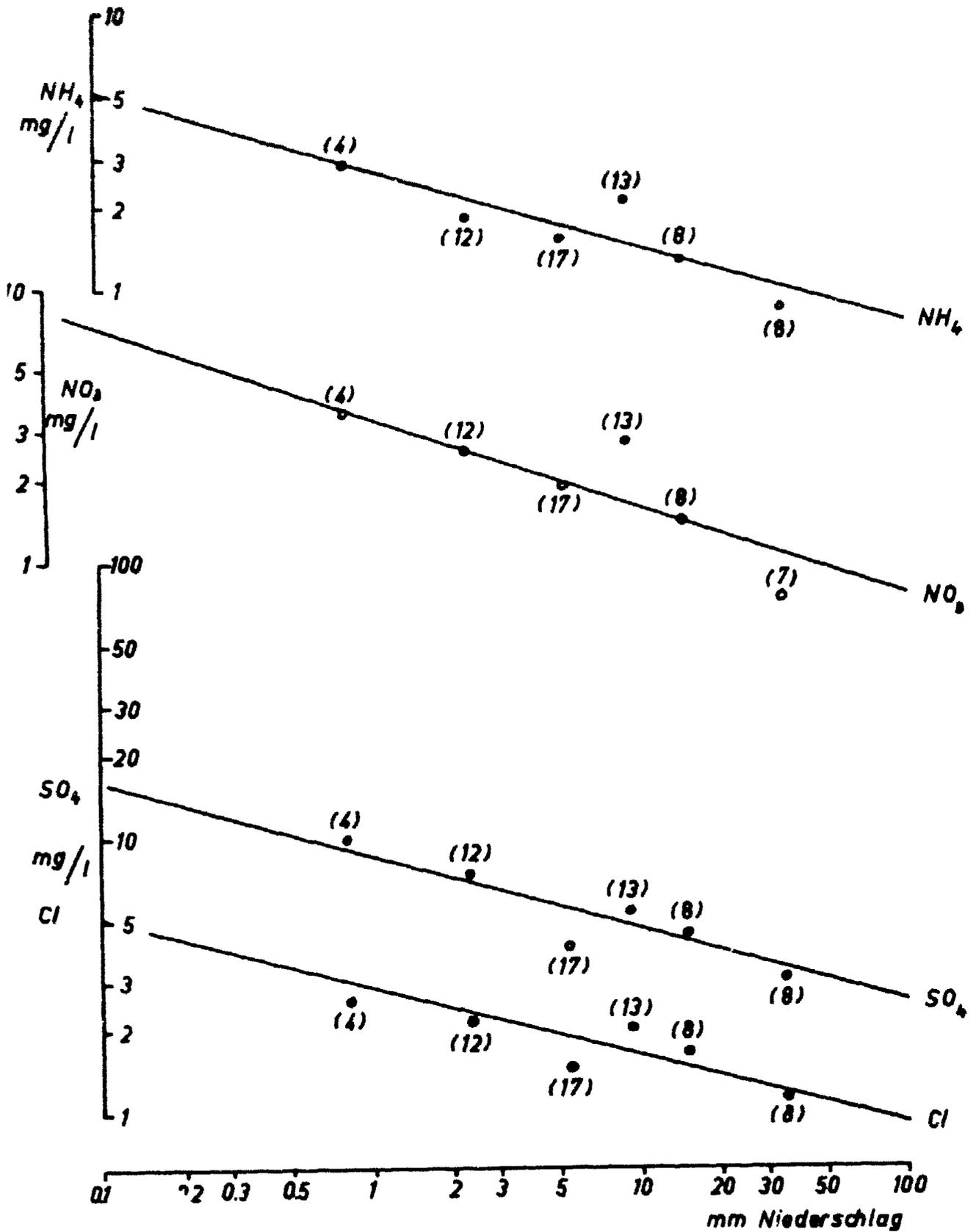


Fig.

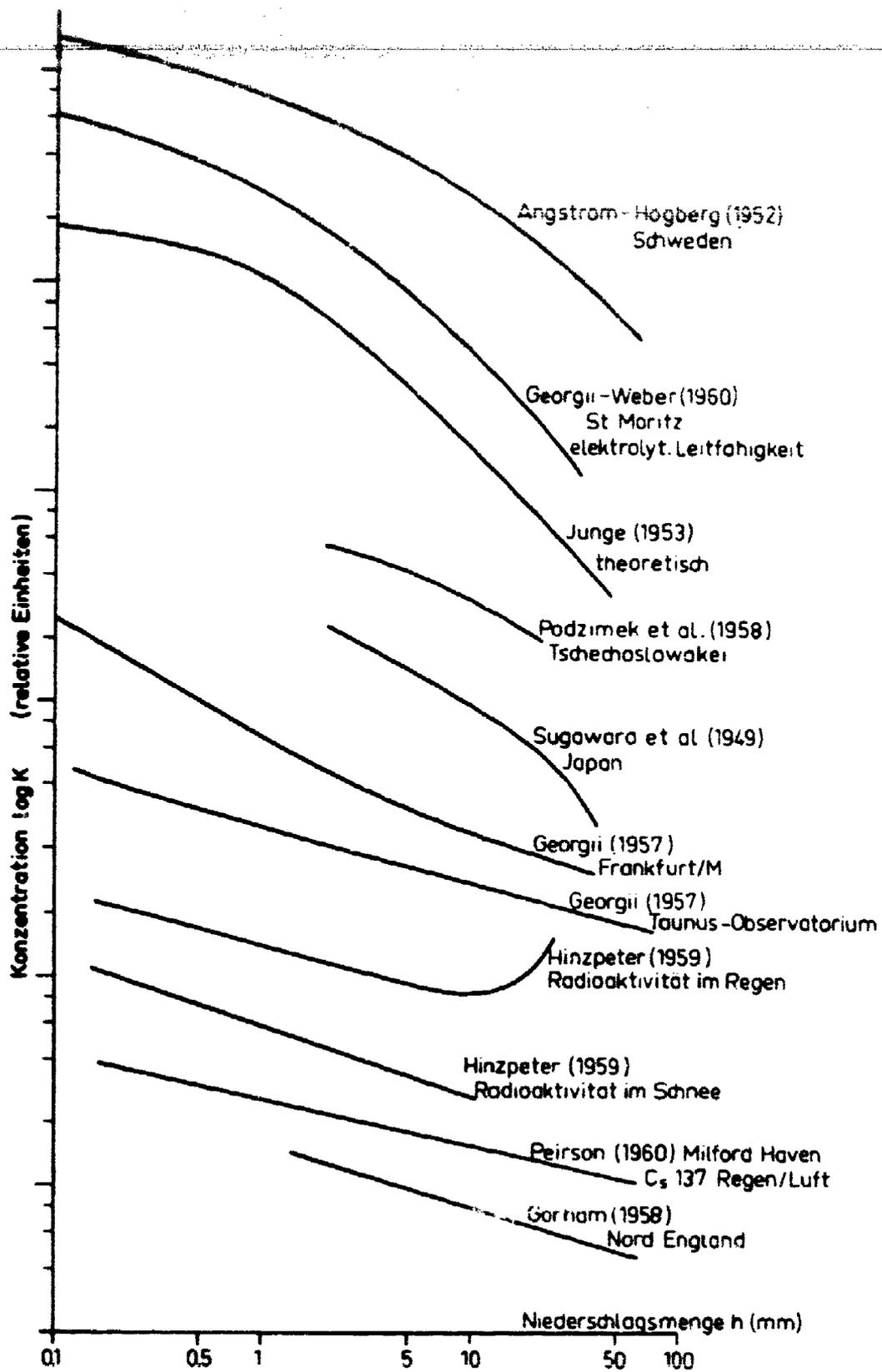


Fig.12

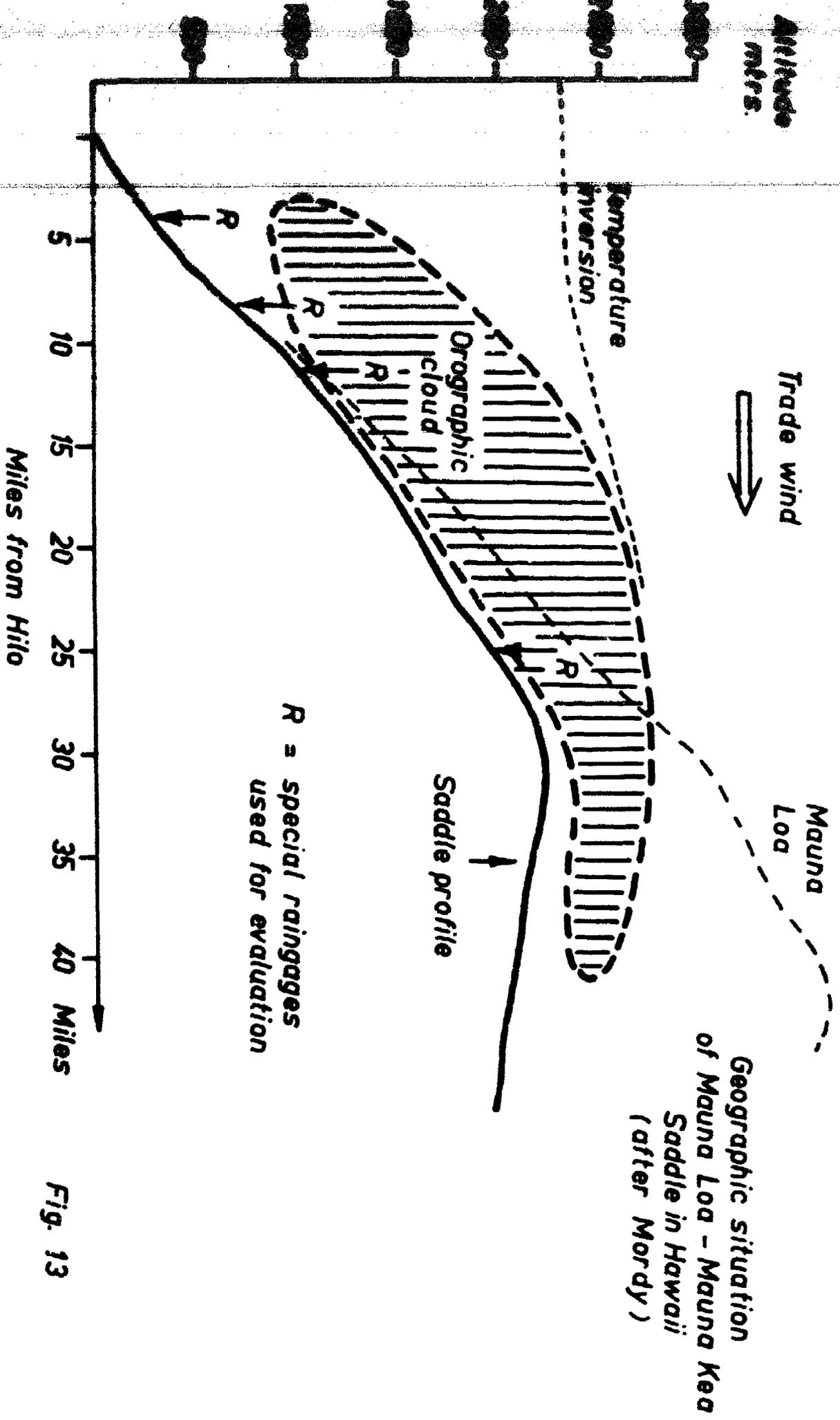


Fig. 13

**Distribution of the chemical composition
of rainfall in Haver**

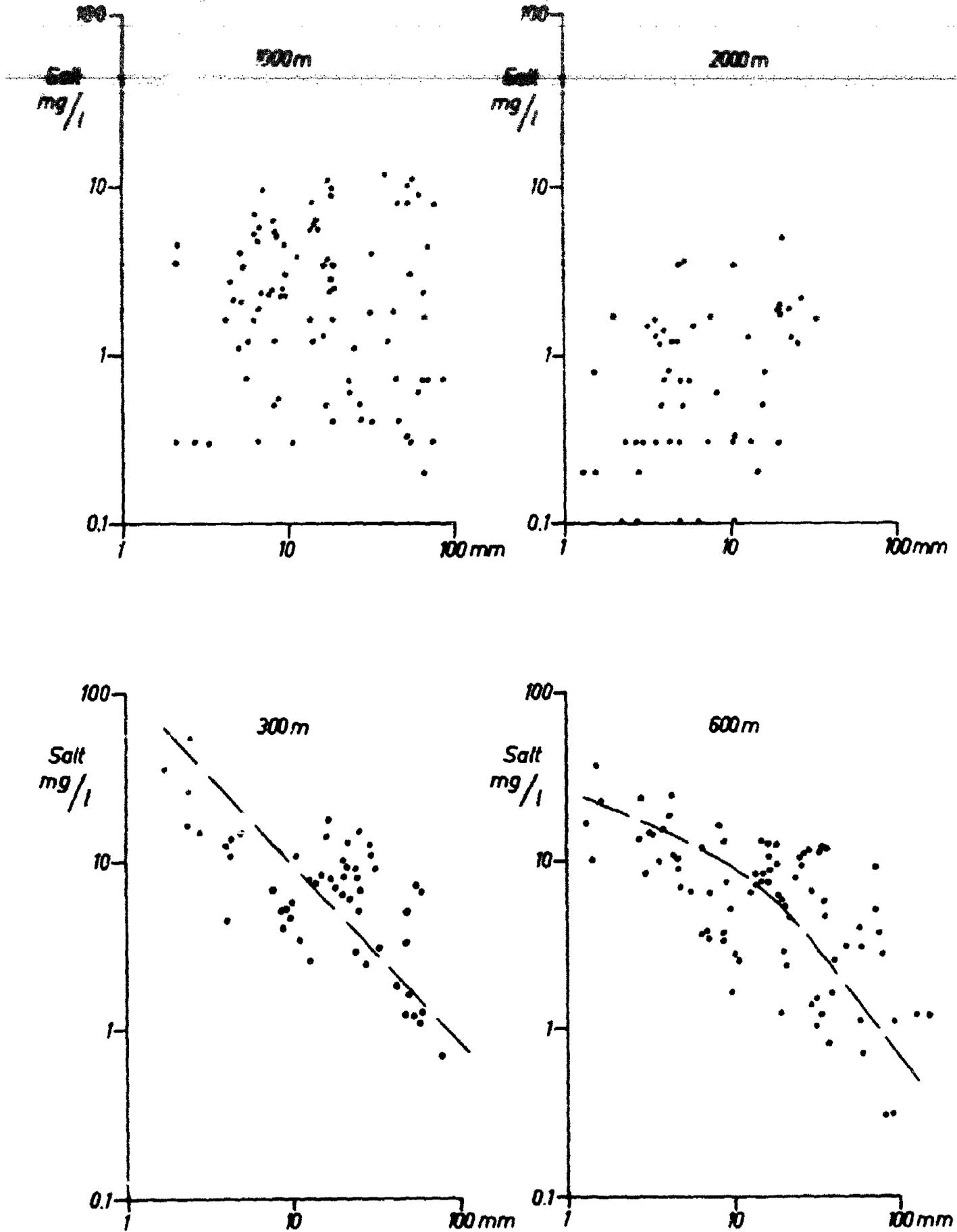


Fig. 14

Chemische Analyse von Einzelniederschlägen Zugspitze, April 1961-April 1962 (Probe 1-156)

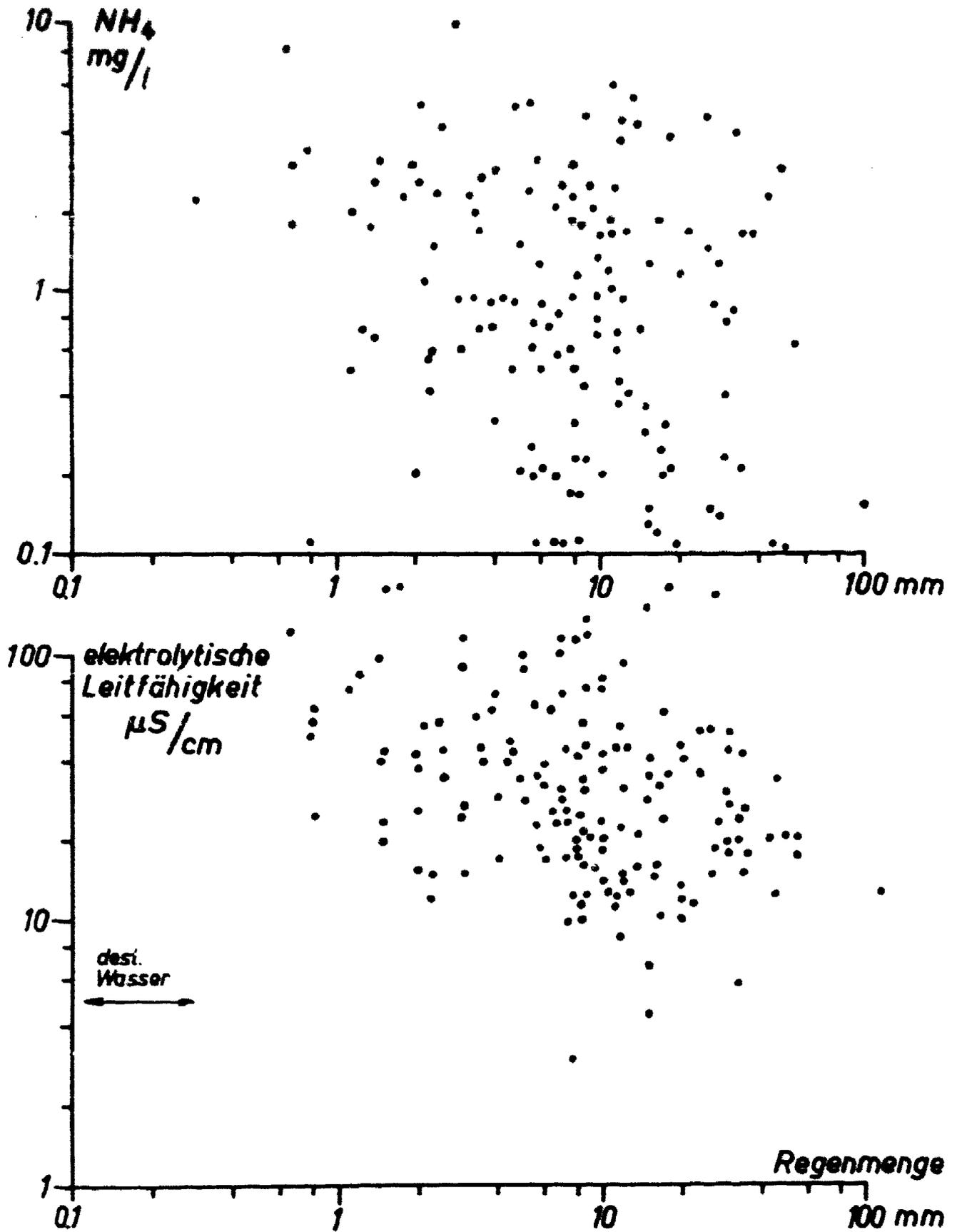
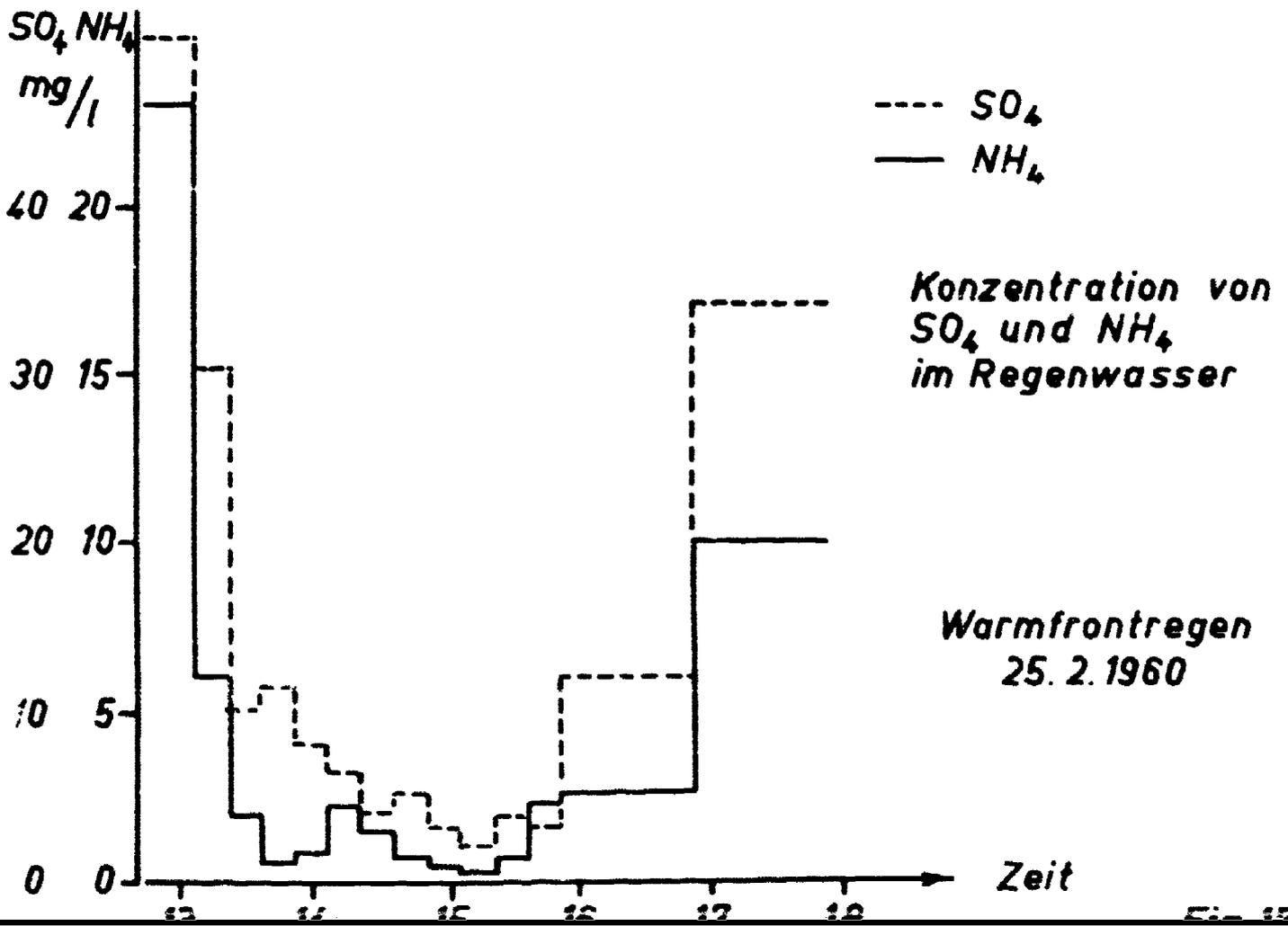
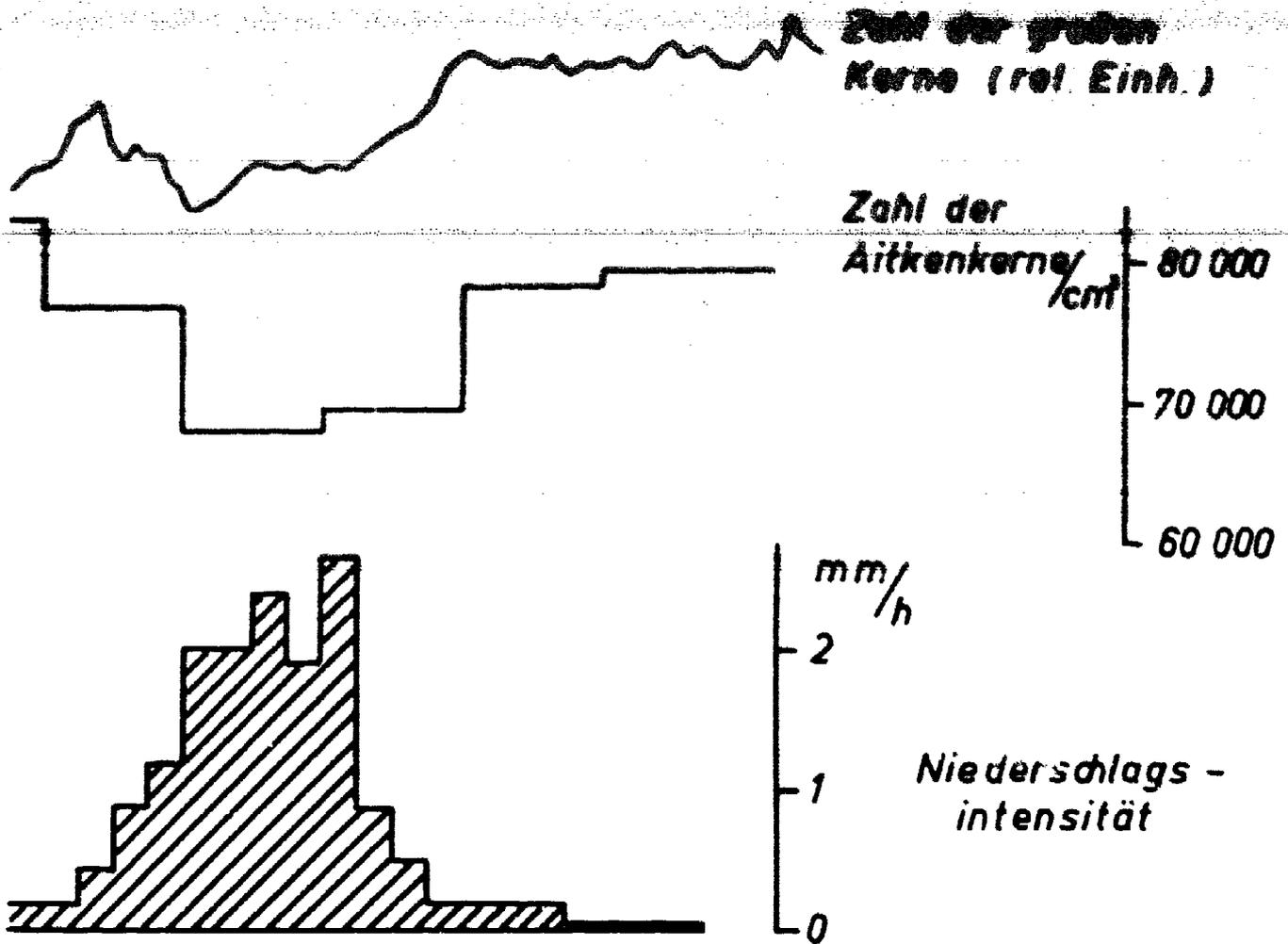


Fig. 1!



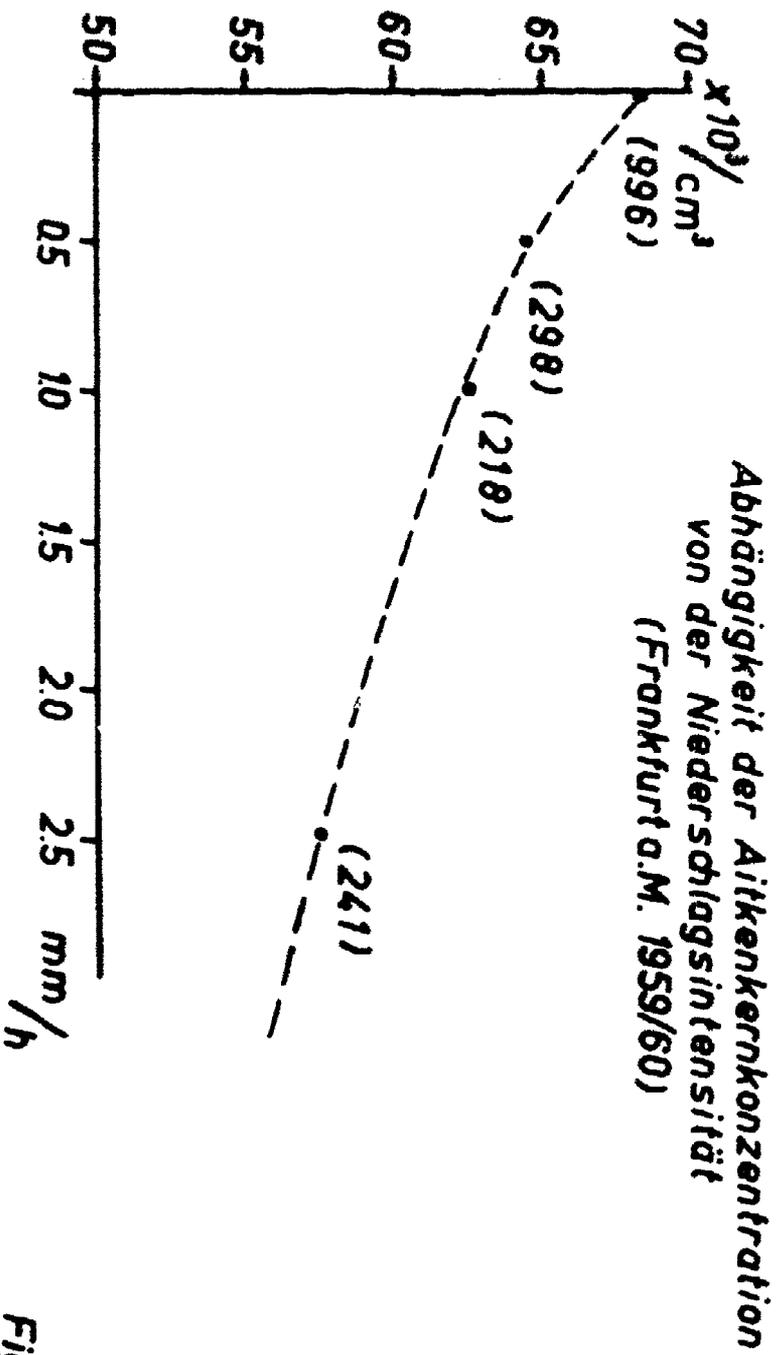


Fig. 18

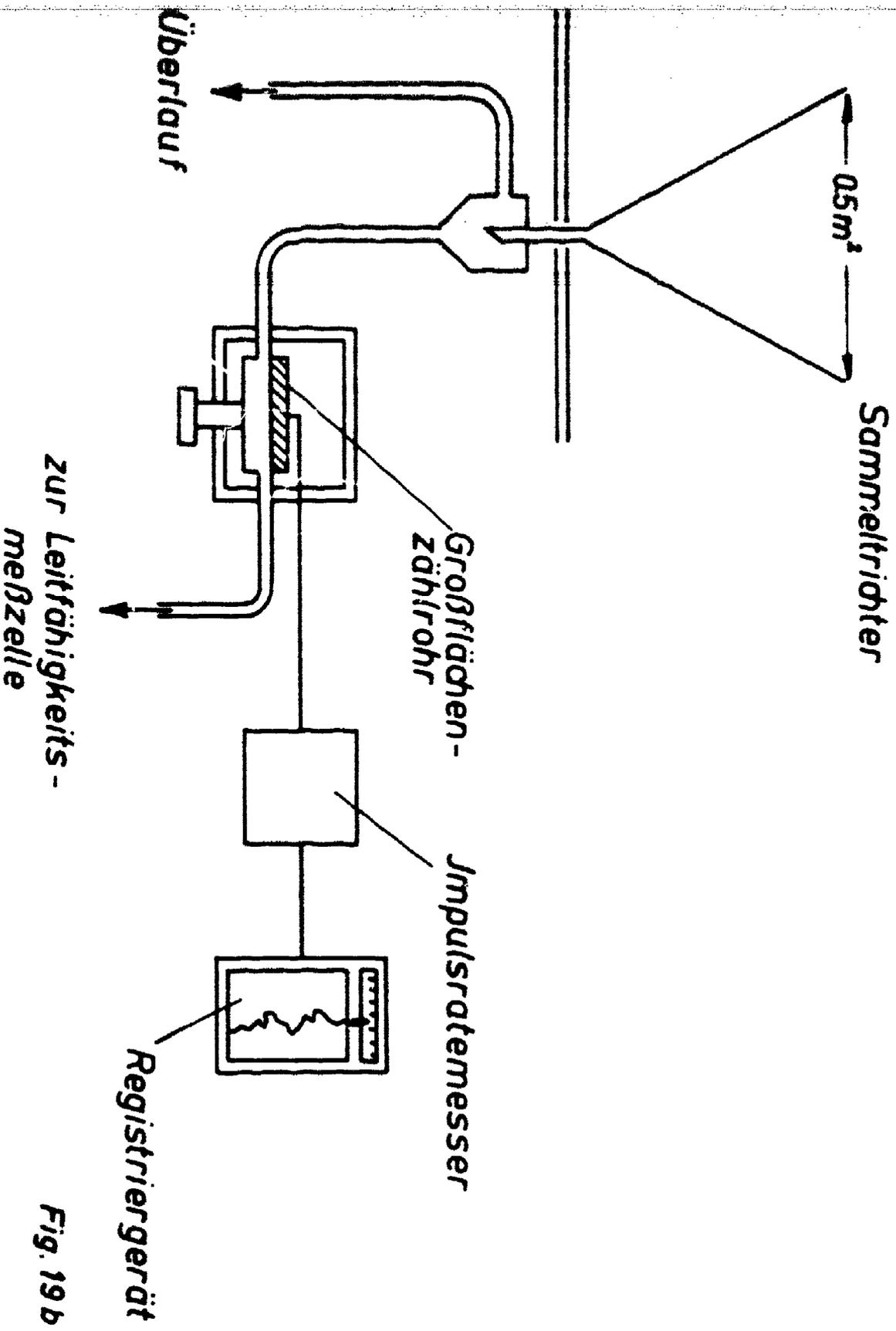
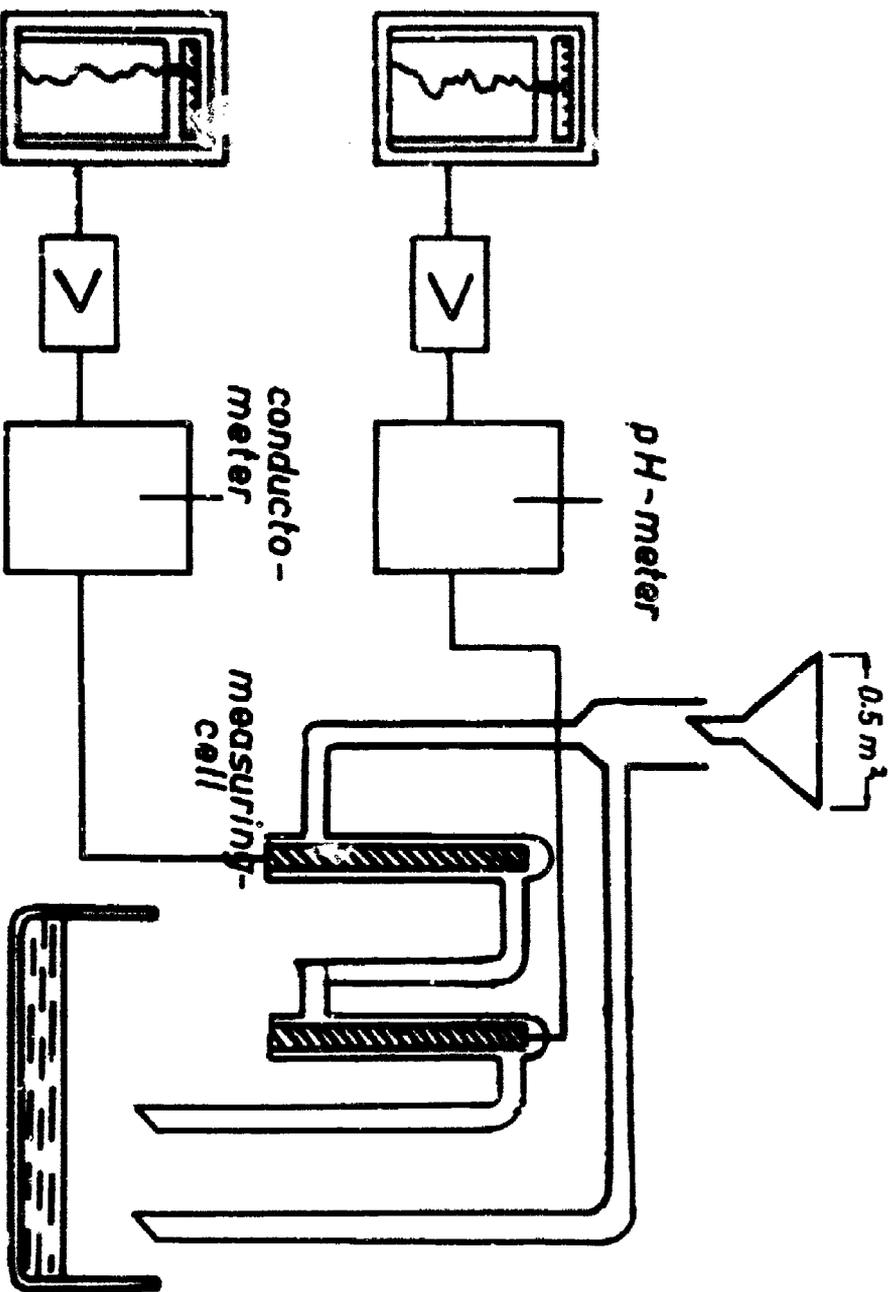
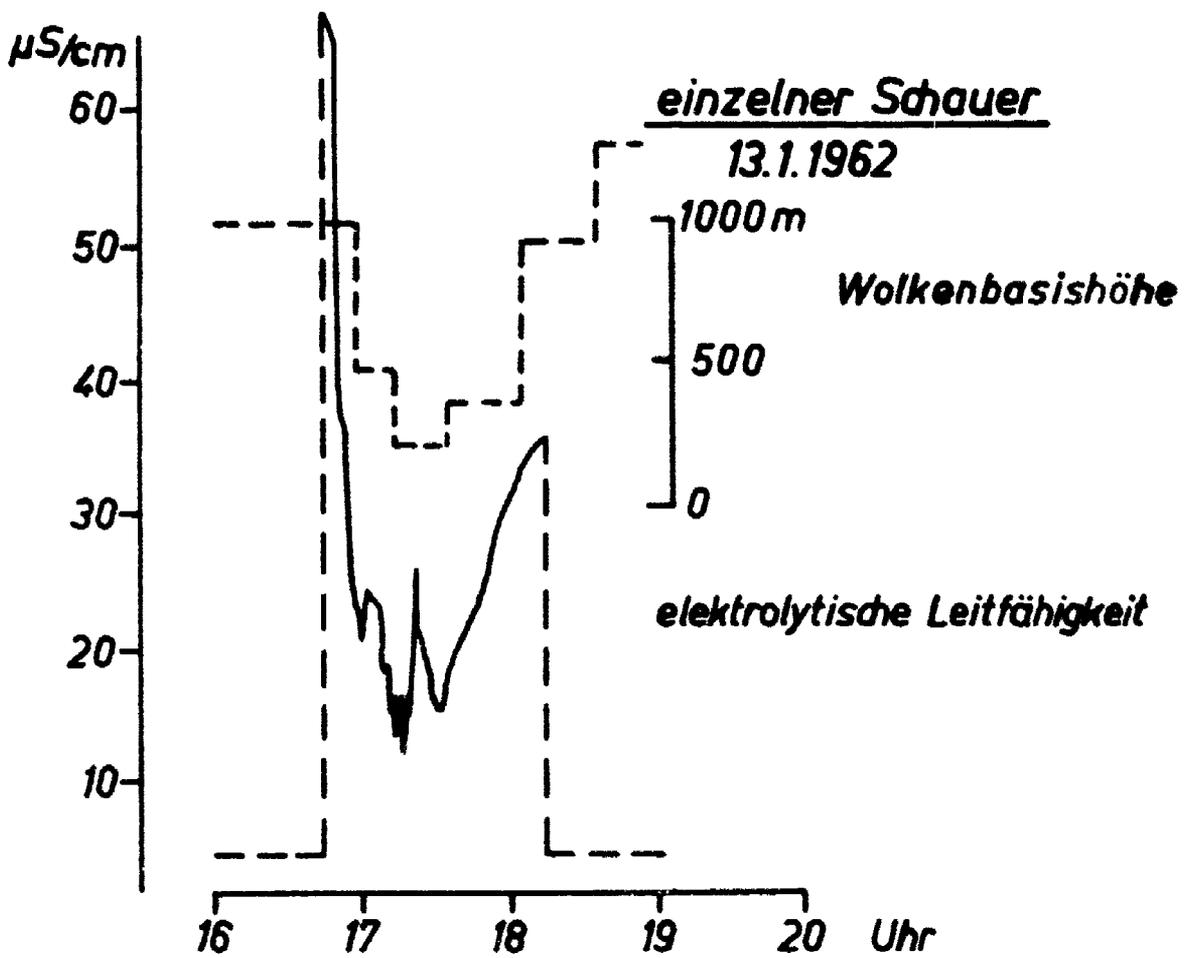
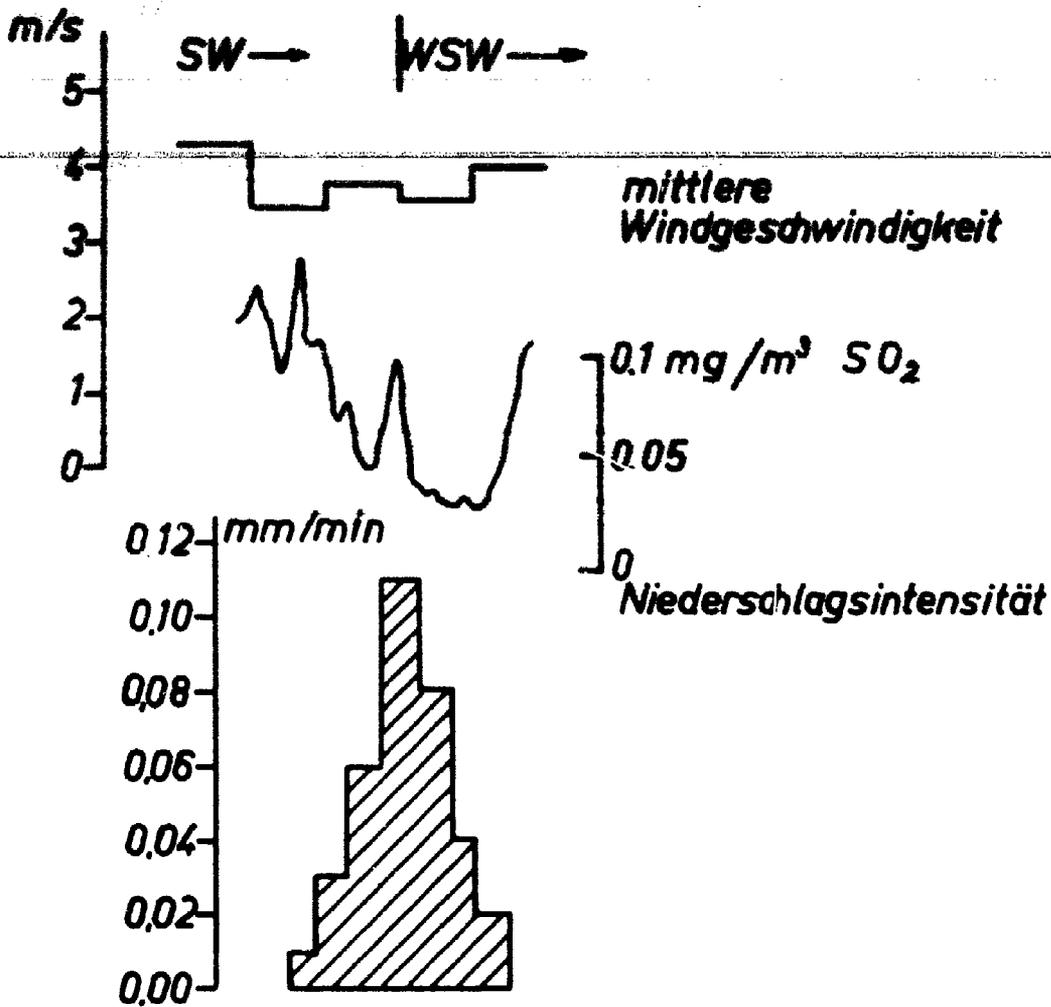


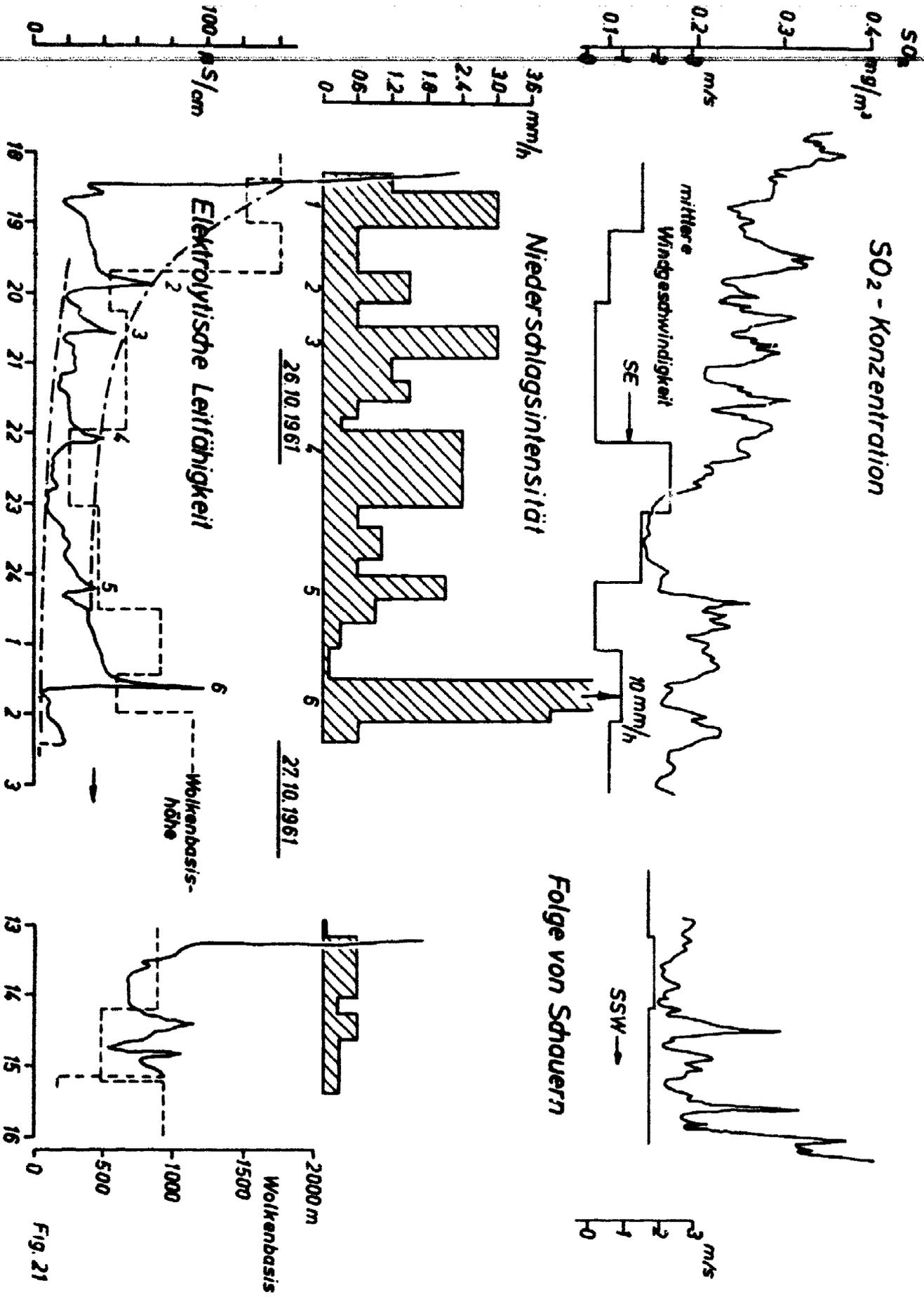
Fig. 19b



*Schematic diagram
of continuous recording
of conductivity-meter
and pH-meter*

Fig. 19a





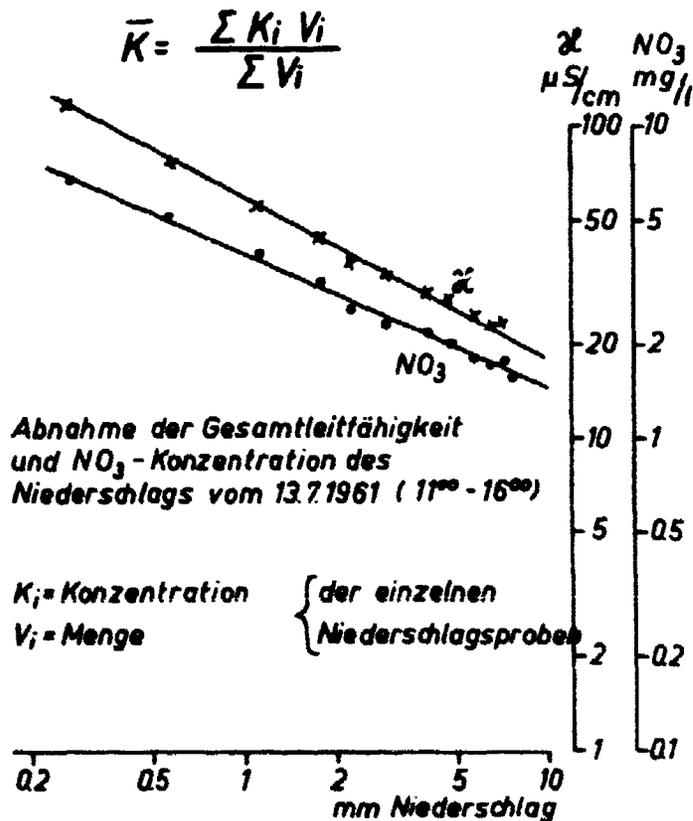
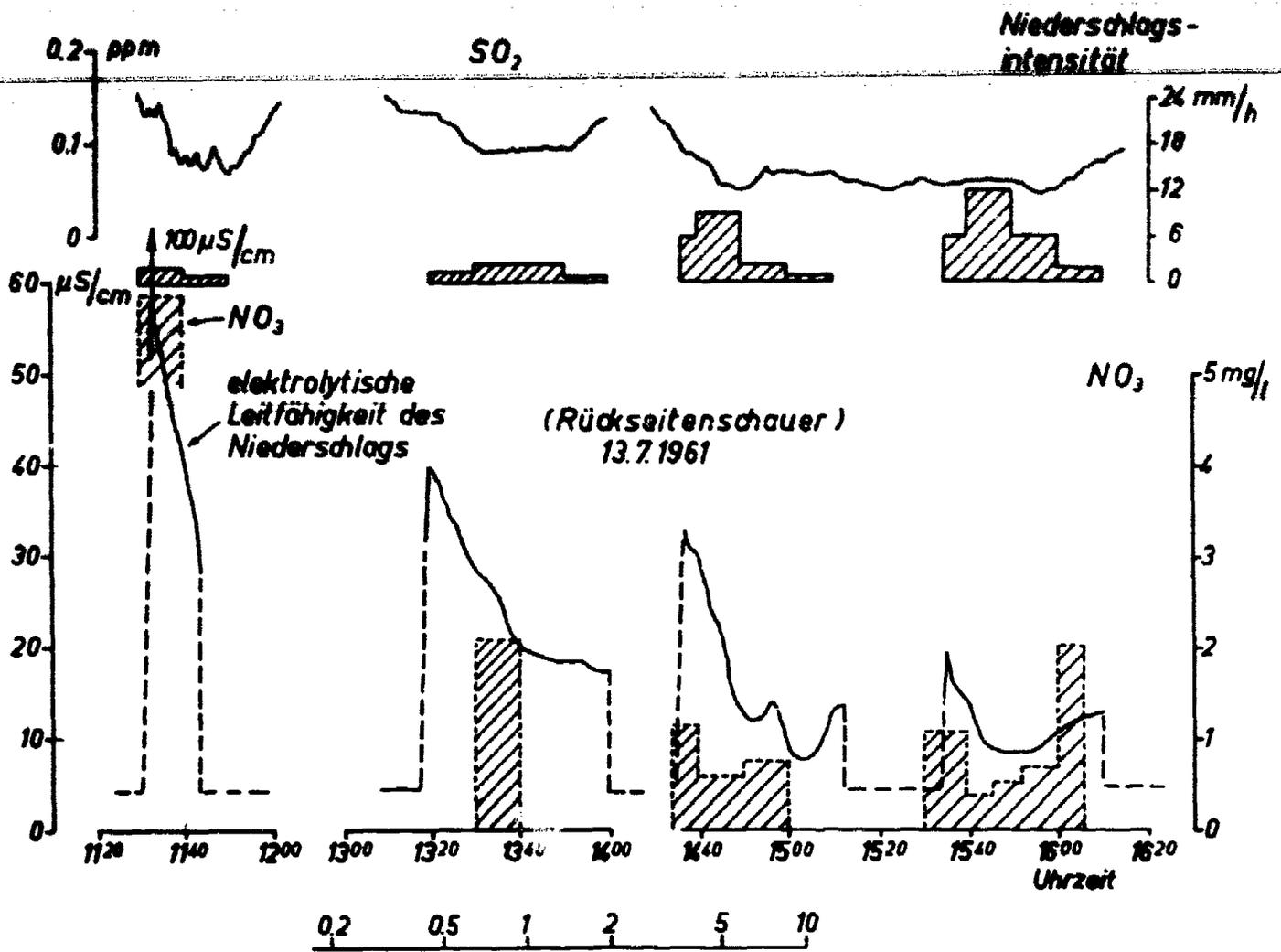
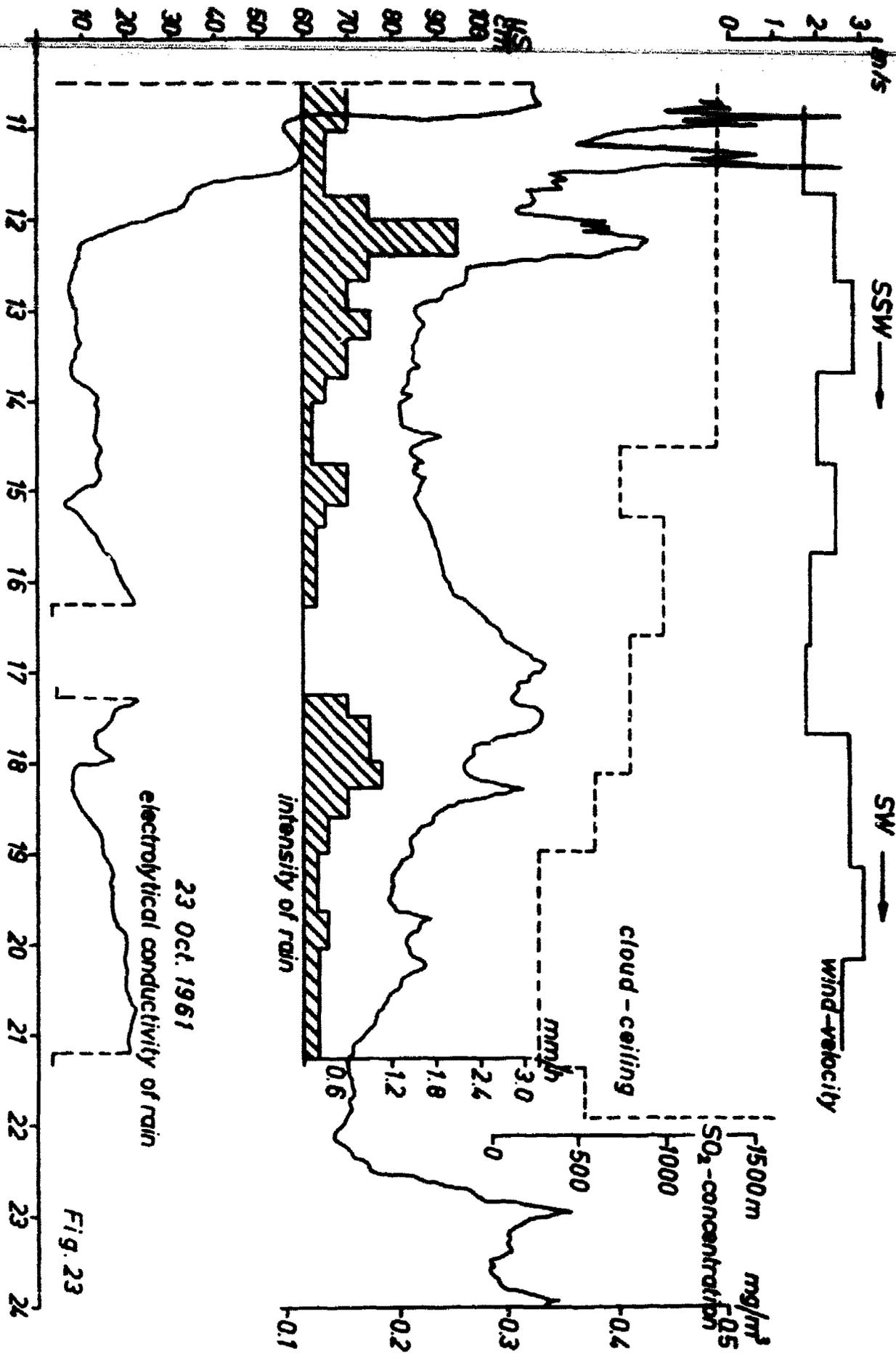


Fig. 22



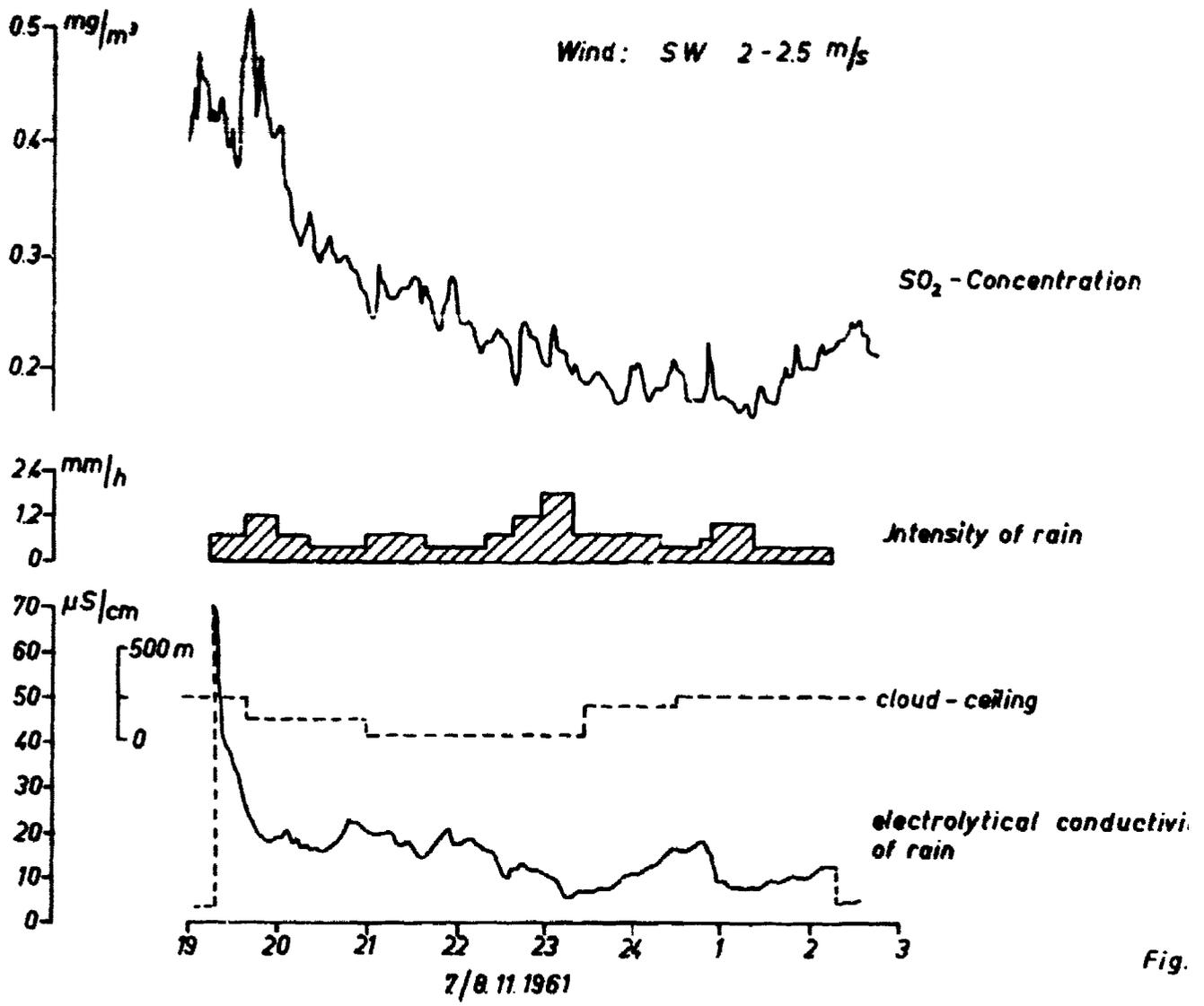
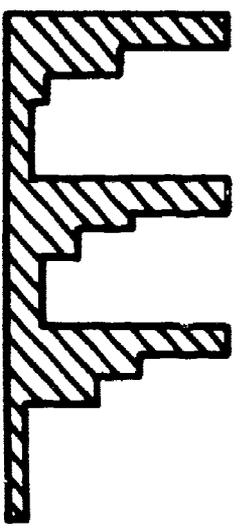
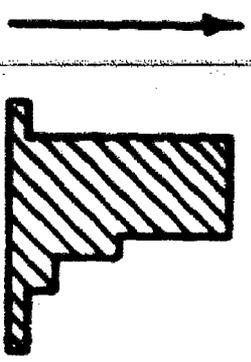


Fig.

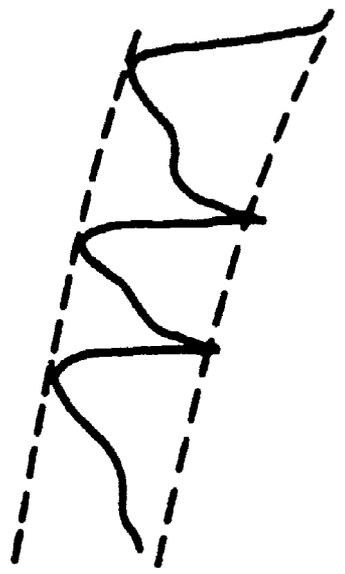
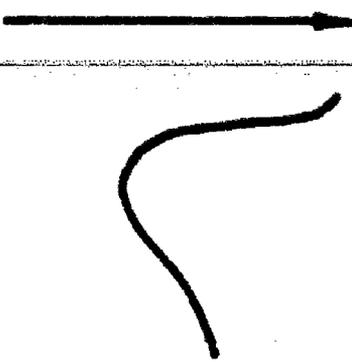
Schematische Darstellung des Zusammenhanges zwischen Intensität und Spurenstoffkonzentration des Niederschlages

I Einzelschauere II Folge von Schauern III Aufgleitregen

mm/Std



mg/l



≤ 1 Stunde

wenige Stunden

> 3 Stunden

Fig. 25

before after
the onset of rain

Budget of
trace-substances
in rain-water

dilution

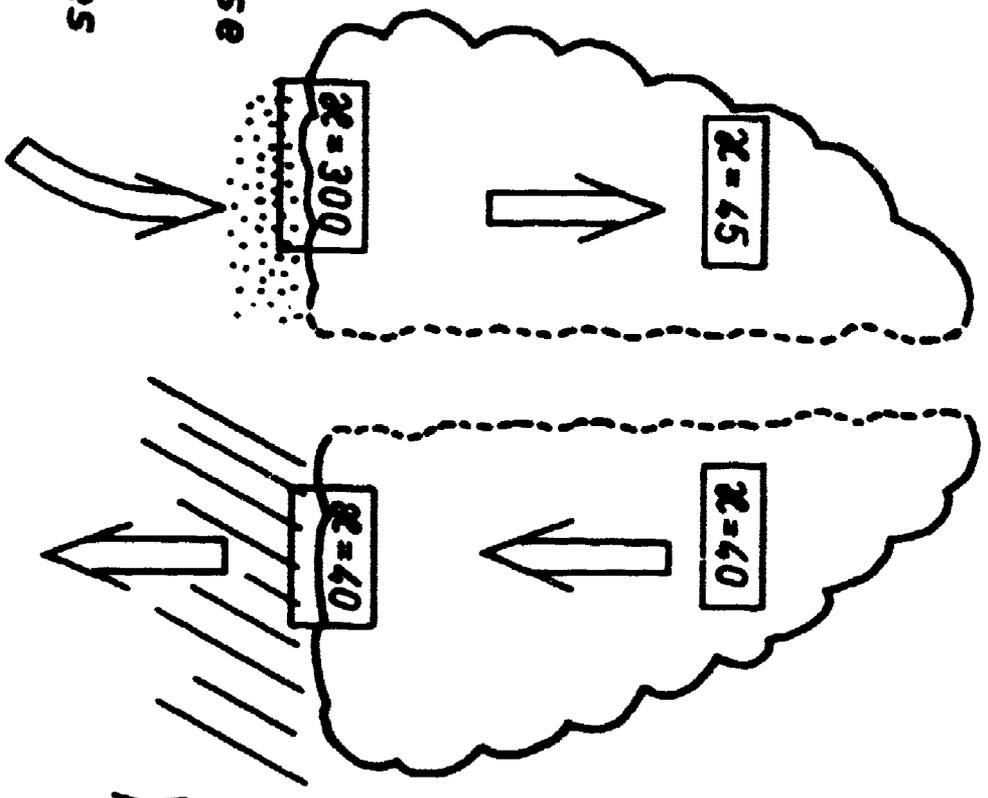
coalescence

condensation
and attachment
of particles

accumulation
at the cloud-base
transport of
trace-substances

wash-out
partial evaporation

\mathcal{K} = elec. conductivity
 $\mu\text{S/cm}$



Earth-surface

Fig. 27

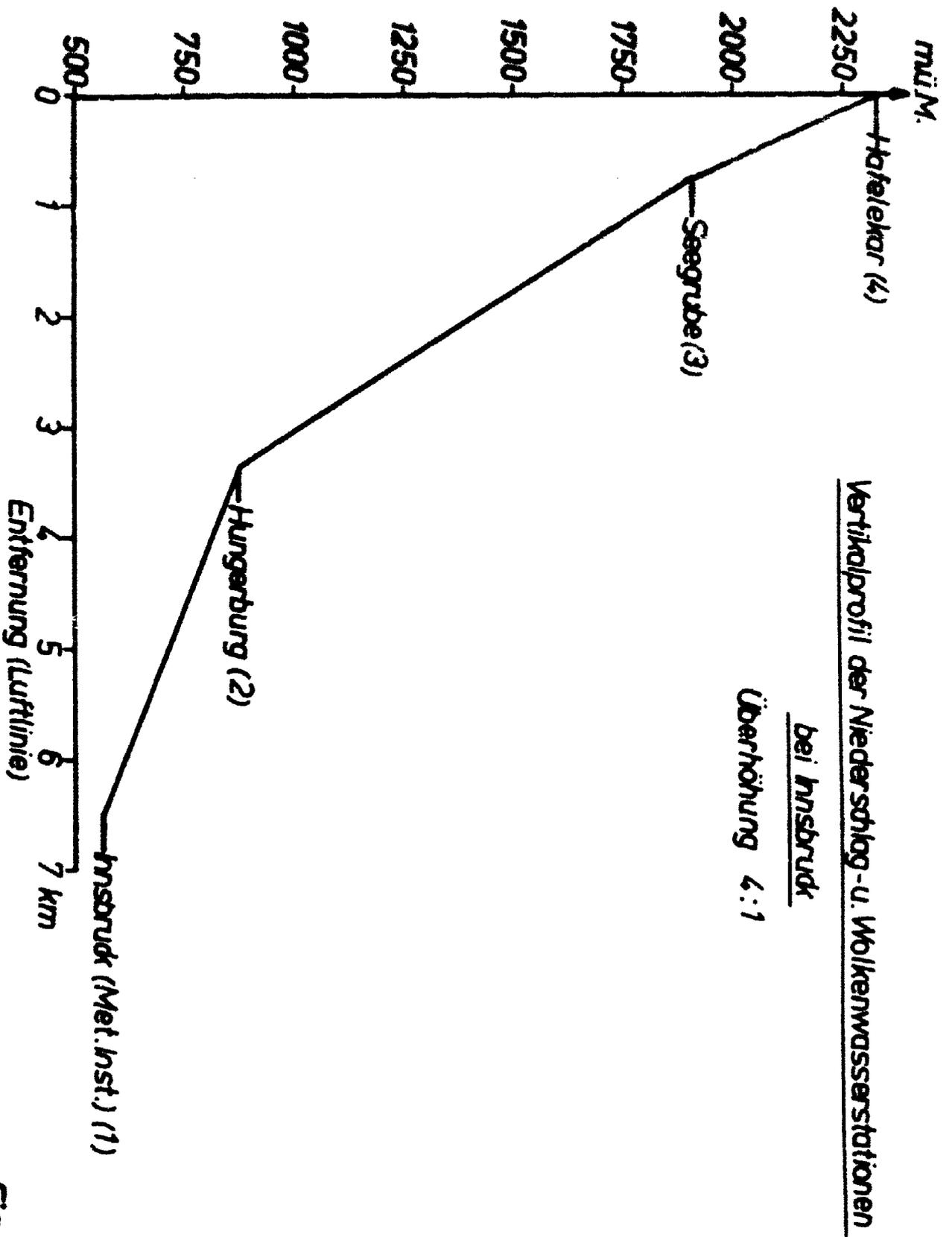


Fig. 28

