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**Investigations on tropospheric
wash-out**

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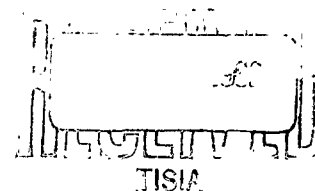
Johann Wolfgang Goethe-Universität
Institut für Meteorologie und Geophysik

Annual Report No. 2

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Investigations on tropospheric wash-out

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I. Abstract

The following report summarizes the results of investigations on aerosol- and trace-gas rain-out and wash-out by cloud- and rain droplets carried out. These investigations were performed during last year at four different locations, namely Frankfurt/Main, Taunus observatory, Mt. Kleiner Feldberg, observatory on Mt. Zugspitze and at St. Moritz, Switzerland. These stations show a wide variety with respect to altitude, climate, supply and production of atmospheric trace-substances. Besides the chemical analysis of individual rainfalls, gaseous traces and aerosols were also micro chemically analysed. During the second stage of our investigation a detailed picture of individual rainfalls was gained by continuous records of the variation of certain components during rainfall.

II. Introduction

The increase of the concentration of anthropogeneous industrial and radioactive aerosols in many parts of the world but also the investigation of the budget of natural atmospheric trace substances - aerosols and gases - demands an investigation of the removal of these traces from the atmosphere to the ground. With other words our aim is an investigation of the self-cleaning process of the atmosphere.

In the following chapter a brief qualitative survey of the different processes leading to a decrease of the aerosol- and trace-gas-concentration of the atmosphere will be given. In this connection we will not consider turbulent mixing and advection of air masses because these processes do not remove trace-substances from the atmosphere but lead only to local changes of the concentration of trace-substances within the atmosphere.

III.1) The removal of trace-substances from the atmosphere

Considering the different processes of removal we have to distinct generally between the processes effective within clouds and during cloud formation and those effective below the cloud-base. Besides this we have to pay attention to the fact that the concentration of gases in the atmosphere is about five to fifty times higher than that of aerosols (both expressed in terms of micrograms/m³). In the schematic diagram Fig. 1 we have entered the different processes leading to a removal of aerosols and gases from the atmosphere.

It can clearly be recognised that within the clouds aerosol-particles are consumed as condensation-nuclei (freezing-nuclei) while other particles are attached on the surface of the cloud droplets by diffusion. It can be seen that these processes are only effective for particles of very discret size-range. According to investigations by Yamamoto and Ohtake as well as by Kuroiwa only a certain fraction of particles below 0.5 μ radius is consumed as condensation-nuclei during cloud-formation. These authors give the following figures:

Fraction of particles of certain size activated as condensation-nuclei

	Radius in micron				
	0.1-0.2	0.2-0.4	0.4-0.6	0.6-1	1-2
Yamamoto and Ohtake	0.4%	2%	17%	60%	100%
Kuroiwa	0.2%	1.7%	15%	24%	100%

If these data are generally applicable only the giant-nuclei are fully consumed as condensation-nuclei.

Below the cloud-bases giant-particles of more than 2μ radius are washed-out by impaction to the falling rain-drops and only very large particles of more than 20μ -radius are removed by sedimentation. Soluble gases are absorbed within clouds and below the cloud base by the cloud-resp. rain-droplets. Fig.2 shows the different size-ranges of aerosols and the way in which they are influenced by the different removal processes. The mechanism of rain-out and wash-out leads to a partial removal of aerosols from the atmosphere and can therefore very well be compared with the retention of aerosol-particles in a mechanical filter. Comparison of the calculations by Greenfield (1) and Hess (2) on the effect of wash-out on particles of certain size with the measurements by W. Jacobi (3) on the retention-efficiency of fibrous aerosol-filters give very similar results. In both cases the Aitken-nuclei are removed by diffusion and the giant nuclei by impaction to the cloud or rain drops resp. to the fibres of the aerosol-filter. In both cases the size-range of the large nuclei are the most resistant particles against the removal from the atmosphere. Upon the efficiency of the absorption of trace-gases we have not yet many quantitative data. The results of our investigation gained so far suggest however that the trace-gas absorption is an important process for precipitation-chemistry. More details will be given below.

Summarizing we can state that an investigation on wash-out processes should aim to separate the following mechanism: Quantitative analysis of the processes within the cloud and those below the cloud-bases as well as separation of aerosol- and trace-gas absorption.

2) The accumulation of trace-substances in rain-water

The attachment of aerosols as well as the absorption of trace-gases to cloud- and raindrops leads to an accumulation of trace-substances in cloud- and rainwater. The concentration of traces in rainwater depends on the supply of aerosols and gases but also on the amount of precipitable water. In Fig. 3 we present a schematic diagram of the presumed mechanism of accumulation of trace substances in rainwater. Aerosols and trace gases are transported by convection from the ground-layer into higher layers of the atmosphere frequently accumulated below the cloud base. Within the cloud near the cloudbase particles are consumed by condensation and coagulation into the cloud droplets. When the cloud-droplets are carried upwards in higher layers of the cloud, the droplets grow by further condensation and coalescence but the concentration of chemical traces in cloud-droplets decreases sharply due to the reduced supply of aerosols and gases in higher regions of the clouds. With the beginning of the precipitation the rain droplets fall again through layers with higher concentration of trace-substances whereby the impactation of particles during the fall increases once again but this time only slightly the chemical concentration of rainwater.

This discrepancy between high concentration of chemical traces in cloud-water near the cloud-base and much lower concentrations found in rain-water on the ground is reflected by our simultaneous measurements of cloud-water and rain-water sampled on our Taunus observatory Mt. Kl. Feldberg in 800 mtrs. altitude. On days when the summit of Mt. Kleiner Feldberg was within the cloud (but near the cloud-base) and when it was raining at the same time we sampled rain-water and separately cloud-water. The chemical concentration of the cloud-water samples is 8 to 11 times higher than that of the rain-water

samples collected at the same location and same time. This result is an expression of the fact that the cloud-water is diluted during the effectiveness of the precipitation-mechanism and that the cloud can be regarded as a kind of filter collecting aerosol-particles from the ascending air-stream and accumulating the trace-substances in the lower part of the clouds. This effect is illustrated in Fig. 4 by some examples taken from the Literature. We have plotted the aerosol-concentration in cloud-free air and within clouds according to measurements by A.H. Woodcock (4), H. Weickmann (5) and M. Röttschke and Mildner (6). Woodcocks measurements of the concentration of salt-particles in cloud-free air and within clouds show a considerably higher concentration of salt-particles in the lower part of the cloud with sharp decrease of the salt-contents in the middle and higher part of the cloud. Measurements in the cloud-free environ-air showed distinctly lower salt-concentrations than were found in clouds. W. Weickmanns measurements of Aitken-nuclei indicate in the same manner layers of high Aitken-nuclei numbers within the clouds, higher concentration than were found in the environ of the clouds. Measurements of large nuclei made with an impactor during balloon ascents in Germany by Mildner and Roetschke revealed a high concentration of large particles in the region of the cloud base which dropped with increasing altitude when the balloon reached higher cloud-levels. The particle-number at the cloud-bases was in many cases higher than that in the ground-layer of the atmosphere. The results of these authors prove the supply of atmospheric trace-substances from the ground to the cloud-base and the accumulation of aerosols in the lower region of the cloud, they also support our findings of high concentration of chemical components in cloud-water collected near the cloud-

base. In this connection measurements by H. Byers, J.R. Sievers and B. Tufts (7) must also be mentioned. Analyses of the composition of different aerosols particles sampled during research flights in different altitudes in the U.S.A. show clearly the formation of layers of higher concentration in certain altitudes above the ground. Byers results are another indication for the transport of aerosols from the ground to higher regions and their accumulation in certain layer formations.

3) Gaseous components and the chemistry of rain-water

On the basis of our simultaneous measurements of gaseous traces, aerosols and chemical components in rain-water carried out at different stations in different altitudes (Frankfurt/M, Kleiner Feldberg/Taunus mountains, Zugspitze/German Alps, St. Moritz /Swiss Alps) we have plotted in Fig. 5a and 5b a schematic vertical distribution of NH_4 - and NO_3 -component found as gas, aerosol and in rainwater. We have also entered the number of large nuclei (dashed line). We have entered the concentration (abszissa) in a logarithmic scale, the altitude (ordinate) in a linear scale. The vertical distribution is only tentative since it must be considered that the horizontal distances between the different stations is quite large. The Fig. 5a shows the decrease of NH_4 in aerosols following an exponential function and it parallels exactly the decrease in number of particles. This result permits the conclusion that the NH_4 -concentration of the atmospheric aerosols is distributed equally independent of altitude. This suggests again the importance of the NH_4 -component in continental aerosols. Of still greater importance in connection with our investigations on rain-chemistry seems the result that the decrease of NH_3 as gas and NH_4 -concentration in rain run almost parallel. We can also state that the trace-gas concentration in higher layers of the atmosphere

is more or less constant compared with the strong decrease of aerosols. Regarding the NO_3 concentration in aerosols, as gas and in precipitation we find the same relation between gas phase and concentration of the same component in rain-water. This parallel trend between gaseous component and chemical behaviour of rain-water indicates important consequences for precipitation chemistry. The relation between the concentration of soluble trace-gases in the atmosphere and the contents of the respective components in precipitation is quite tight over the continent. The ratio of trace-components in rain and gaseous components in the atmosphere is nearly constant. This fact is illustrated in Fig. 6 showing the ratio of concentration of trace substances in rain (mg/l) and trace-gases in the atmosphere ($\mu\text{g}/\text{m}^3$) for five continental stations. (The values for Ultuna/Sweden are results taken from Tellus). It can be easily recognised that the fluctuations of this ratio at continental sampling-sites are very slight. If the ratio is considered between the concentration of trace substances in rain and the concentration of aerosols the values of this quotient fluctuate very strongly from one sampling station to the other and no general relation whatever can be found. The results entered in Fig. 5 and 6 stress the importance of gaseous traces for precipitation chemistry, they can be interpreted in that way that at locations with high concentration of trace-gases in the atmosphere the concentration of trace substances in rain-water is also high and vice versa. In this connection it is again important to state that the concentration of trace gases is generally five to fifty times higher than the concentration of the same components fixed in aerosol particles (Both concentrations expressed in terms of micrograms/ m^3). Maritime stations show a quite different behaviour, the ratio between the concentration of trace substances in rain and trace gases in the

atmosphere fluctuates considerably at maritime sampling stations. This is probably due to the fact that the gases considered here are of continental origin. With regard to Fig. 5a and 5b we finally want to mention that a sharp decrease of the aerosol-concentration with altitude and a comparatively small decrease of the trace-gas concentration with altitude was also found by C. Junge (8) in the courses of his measurements in Hawaii. A more detailed description of Figs. 5a and 5b concerning problems of air-chemistry has been given by H.W. Georgii elsewhere (9).

4) Influence of the quantity of precipitation on the concentration of trace substances in rain-water

During the first part of our investigations of individual rainfalls we have given an analysis of the relation between the amount of precipitation and the concentration of different trace-substances in rain-water. An evaluation of the analyses and a description of the results has been presented in our Technical Note No 1, to this contract (10). In Fig. 10 of Technical Note No 1 we have compared our result gained at Frankfurt/M and on the Taunus observatory at Mt. Kleiner Feldberg (800 mtrs altitude) with the results gained by Angström in North Sweden and with a calculated curve by Junge. In the meanwhile more information on this problem has been gathered which will be presented herewith.

In Fig. 7 of this report we have entered the relation between concentration of trace substances in rain-water (ordinate: logarithmic scale in relative units) and amount of precipitation (abszissa: linear scale in mm). In Fig. 7 we have entered from above to below the relation found by A. Angström and L. Högberg (11). Our own results gained at Frankfurt/M.

and at the Taunus observatory as described in detail in (10), below these curves the results gained by M. Hinzpeter, F. Becker und H. Reifferscheid (12), and those of D.H. Peirson, R. Crooks and E.M. R. Fisher (13). The both last mentioned curves represent the relation between radioactive fall-out attached to rain-droplets and the amount of precipitation. The results of the last named authors show good agreement with our own results gained at Mt. Kleiner Feldberg on the chemical composition of rainwater independance of the rate of precipitation. This suggests that the accumulation of radioactive fission products in rainwater and of natural trace substances obey the same law. The curve given by Hinzpeter and collaborators shows an increase of concentration with very high amounts of precipitation (above 10 mm/day), which we will not discuss here. It can therefore only be compared with our measurements for rainfalls below 10 mms. In a recently published report E. Martell (14) gives results of the Sr-90 concentration of Bedford rains which show also good agreement with the curves mentioned so far as regards the decrease of Sr 90 concentration with increasing amount of precipitation. - The dashed curve next to Peirsons results represent the analyses which one of us (E. Weber) made at St. Moritz/Switzerland during summer 1960. Here the electrolytical conductivity of the rain water of individual rainfalls was measured. We have entered this curve as a dashed line because the results ^{can} only be considered tentative being based only on 14 individual cases. These investigations at St. Moritz are continued during summer 1961. The decrease of the electrolytical conductivity of rain water with increasing amount of rainfall at St. Moritz shows the same features as Angströms curve from North Sweden and as Junges theoretical curve considering only wash-out without further supply of additional trace-substances during the rain.

Junges theoretical curve also neglects the processes of attachment of particles to cloud-droplets taking place within the cloud.

In addition to the results entered in Fig. 7 we have reanalyzed the measurements of precipitation carried out in Hawaii while the investigations of project "shower" took place in 1955. Fig. 8 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 (15). Along the Saddle Road and the Kulani Road leading to the saddle between Mauna Coa 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 (16). 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. 8 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. 9. In Fig. 9 we have entered the salt content of rainwater (in mg/ltr) in dependance of the amount of precipitation (in mms), both in logarithmic scale. We find that at 700 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. 7) 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 preci-

precipitation in 1000 and 2000 mtrs. altitude. That means at those stations located within the orographic cloud resp. at its base. At these two stations the precipitation was collected within the cloud where it was produced and obviously in these 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 to 1 August 1961 48 samples of individual rainfalls were collected on the Zugspitze and analyzed in our laboratory. Some of the analyzed components are entered in Fig. 10. The NH_4 -concentration of Zugspitz-rain as well as the electrolytical conductivity (expressed in microsiemens/cm) do not show any relationship to the rate of rainfall. The electrolytical conductivity is a measure of the salt content of rain. Similar as the case in Hawaii above 1000 mtrs also on Mt. Zugspitze the summit of the mount is in nearly all cases within clouds when it rains. It may be mentioned that the electrolytical conductivity of Zugspitz-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. 11.

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.

Type III applies to location with only little pollution and therefore negligible supply of trace-substances from the ground. We found this relationship to be applicable for Ultuna/Sweden, St. Moritz/Switzerland and Hawaii (below the orographic cloud). The same shape of curve results also from theoretical considerations by C. Junge (17). In these cases the trace-substance content of the atmosphere is more and more rapidly reduced with increasing rate of rainfall and a quantity exceeding about 5 to 10 mms. leads only to a further dilution of the rain which fell during the first phase.

Type IV On 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 above described investigation shows the influence of location, altitude, supply of trace-substances and amount of rainfall for the accumulation of trace-substances in rain-water. Type IV finally shows that within the cloud all drops have more or less the same concentration of trace-substances.

5) 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 playing together. 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. 12 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 rain-water 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/ccm at the time of the peak rain-intensity.

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. 13 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 to 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 rain-water 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 (18). Interesting information on the fluctuation of trace-substance concentration in rain-water during the course of precipitation was also contributed by W. Jacobi (19). 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 airmass change. According to Jacobis assumptions 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 dense 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.

6) 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. The electrolytical conductivity of rainwater is however an indicator for the total soluble mass of trace-substances in water, therefore for the salt-concentration of water. Up to now this elegant method for measuring the impurities in rainwater has been used only by R. Siksna (20) and A.K. Mukherjee (21). Mukherjee measuring the electrolytical conductivity of Indian Monsoon rain did however not record continuously the time-changes of the conductivity. It was primarily the aim of our investigations to

record continuously the time-fluctuations of the electrolytical conductivity of rainwater during individual cases of rainfall. The method of measurement was the following: A collecting funnel with 0.5 m^2 surface was placed on the roof of the department's building. The collected rainwater is conducted through a polyethylene tube into the cell taking 10 cm^3 of water for measuring the conductivity. The platinum electrodes were coated with a thin layer of platinum chloride to avoid polarization. The resistance of the rainwater is measured with a conductivity-meter manufactured by Dr. A. Kuntze, type KT 3, and continuously recorded. Fig. 14 shows a schematic diagram of the instrumentation for this purpose. The zero-point is marked by distilled water with which the conductivity-cell is normally filled, when it does not rain (electrolytical conductivity: $3-10 \mu \text{ S/cm}$).

As first step we had to ascertain that the measurements of the electrolytical conductivity are comparable with direct analyses of certain chemical components in rainwater. Parallel investigations of the electrolytical conductivity and the cations ($\text{NH}_4^+ + \text{N}_a^+ + \text{C}_a^{++}$) analyzed separately show that there exists a strong correlation between these two components. The same applies to the relation between anions ($\text{SO}_4^{--} + \text{Cl}^- + \text{NO}_3^-$) and the electrolytical conductivity. In the last case the range of fluctuation seems to be broader. This relation is valid for the three locations where we collected rain-samples from April 1961 to September 1961, namely Taunus observatory, Kleiner Feldberg, town of Langen near Frankfurt/M and observatory on Mt. Zugspitze. Fig. 15a and 15b show the relation between electrolytical conductivity and ions analyzed in rainwater. A certain range of fluctuation is to be expected since the ions analyzed by us are only a limited selection of the total number of components dissolved in precipitation.

The following diagrams show some of the records which were recently gained during rainfalls of summer 1961: Fig. 16 shows the course of electrolytical conductivity during a shower connected with the passage of a low pressure cell. Very shortly after the beginning of rain the electrolytical conductivity drops suddenly and some fluctuations of very short period can be observed. The absolute minimum of electrolytical conductivity of precipitation coincides with the maximum of rain intensity at about 16.00 hrs. With decreasing rain-intensity the electrolytical conductivity increases again reaching now a higher value than at the beginning of the rain. This case shows a strong inverse correlation between electrolytical conductivity and intensity of rain. In Fig. 16 we have also entered a record of the SO_2 -concentration at ground-level. SO_2 -concentration was measured with an instrument only recently developed which is applicable for low SO_2 -values. The SO_2 -curve shows a slight drop only at the time of the highest rain-intensity. Some analyses of NO_3 -concentration of rainwater are also entered. The next case plotted in Fig. 17 was gained during a thunderstorm followed by continuous rain of decreasing intensity. Two phenomena are very interesting: 1) the strong fluctuations of the electrolytical conductivity of precipitation during the thunderstorm. These fluctuations can be more clearly seen in the separate figure drawn in the right lower corner of Fig. 17. 2) It is furthermore interesting to note that the general tendency of the variation of electrolytical conductivity shows an increase with time. Actually one should expect a decrease of the electrolytical conductivity with time taking the wash-out effect into consideration. However the influx of fresh air masses and the supply of trace-substances produced during the rain seems to be of greater importance than the concentration of trace-substances which were provided at the beginning of the rain. Again, as in Fig. 16 a strong influence of the rain-intensity can be observed. Minima of the intensity

cause a sharp peak of the electrolytical conductivity and vice versa.

Quite a different picture is presented by the case shown in Fig. 18. This case is a heavy thunderstorm and different showers connected with the passage of a cold-front. In contrast to the cases presented in Figs. 16 and 17 the electrolytical conductivity of precipitation is proportional to the intensity of rain. Particularly during the second phase of the inbreak of cold air masses between 12.00 hrs and 14.00 hrs this can be recognised. The variation of electrolytical conductivity shows an exactly parallel trend with the rain-intensity. During this stage an intensity of 32 mms/hr was reached which is extremely high for European climate. A possible explanation for the parallel trend between intensity and salt-concentration of the rain in the case of the cold-front passage may be that the temperature distribution is vertically very instable, so the clouds are continuously with fresh air-masses supplying a continuous influx of additional trace-substances. This effect will probably be supported by the occurrence of wind shears. Further information must be awaited to gain a more definite conclusion.

Of particular interest is the fourth case which we present in Fig. 19. Here we have measured the electrolytical conductivity of a series of four showers between 11.00 and 16.00 hrs on 13 July 1961. During each of the four showers the electrolytical conductivity of rainwater drops but at the beginning of the consecutive shower it is higher than at the end of the previous one. This indicates fresh supply of trace-substances in the time-interval between two showers. Besides the measurements of the electrolytical conductivity (κ) we have entered some measurements of the NO_3 -concentration in rainwater. The general trend of the NO_3 -variations agrees with that of the electrolytical conductivity. In the upper part of Fig. 19 we have entered 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. 19 we have plotted the net total electrolytical conductivity (and NO₃-concentration) of rain-water independance 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. 19 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 what seems still more plausible 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 (20) in Sweden and A.K. Mukherjee (21) in India reveals that the electrolytical conductivity of Frankfurt-rains is about twice (compared with Siksna) to five times (compared with Mukherjee) higher this being a result of the higher concentration of atmospheric trace-substances in middle Europe.

IV. Final Remarks

For a detailed investigation of the wash-out process of atmospheric trace-substances it is important to separate the processes leading to the attachment of trace-substances to cloud-droplets within clouds from those effective below the cloud-base.

Besides aerosol-particles soluble gas-traces are incorporated into cloud- and rain droplets. Perhaps the absorption of gases by cloud-droplets is more important than that taking place during the fall of the raindrops owing to the difference of residence-time of the droplets, within the clouds resp. during fall. Our simultaneous measurements of aerosols, gas-traces and precipitation chemistry carried out at Frankfurt/M, Mt. Kleiner Feldberg, St. Moritz and Zugspitze hint the importance of gaseous components for the accumulation of chemical traces in rainwater.

Our chemical analysis of individual rainfalls continued during last year and extended to more stations permits to distinguish four different types of relation between the quantity of rain and the concentration of certain chemical components in rainwater. The validity of each of these four relations depends of the location and the supply of atmospheric trace-substances. The difference between type I and type II is caused by the 700 mtr. thick ground-layer of the atmosphere between Mt. Kleiner Feldberg and Frankfurt being an additional reservoir for trace-substances. The difference between type II and type III is caused by the reduced production of trace-substances in North Sweden or the Swiss Alps while type IV relation applies to mountain-station being mostly within the clouds when rain is falling. It seems that a differentiation of the trace-substance concentration of raindrops with regard to the quantity of rainfall takes place only in the cloud free area below the cloud-base and is caused

by wash-out and/or partial evaporation of raindrops.

Detailed analysis of chemical components in rainwater during the course of individual rainfalls and continuous records of variations of electrolytical conductivity during rainfalls reveal the importance of rain-intensity for the accumulation of trace-substances in rainwater and present a detailed picture of the variations of trace-substance concentration in rainwater during individual rainfalls. The dependance of trace-substance concentration from rain-intensity shows clearly that by no means in all cases an amount of rain exceeding 2 mms. leads to a further dilution of the rainwater.

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17, individual cases of rainfall.
18,
19

Aerosole

Spurengase

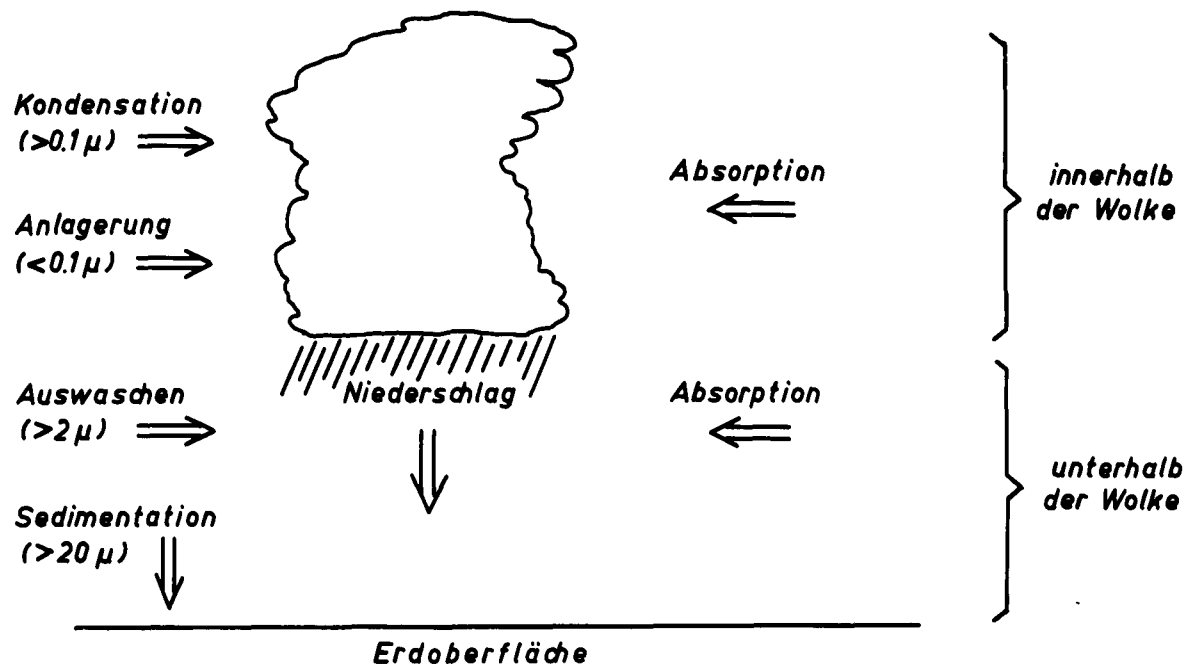


Fig.1

Removal of aerosol-particles from the atmosphere

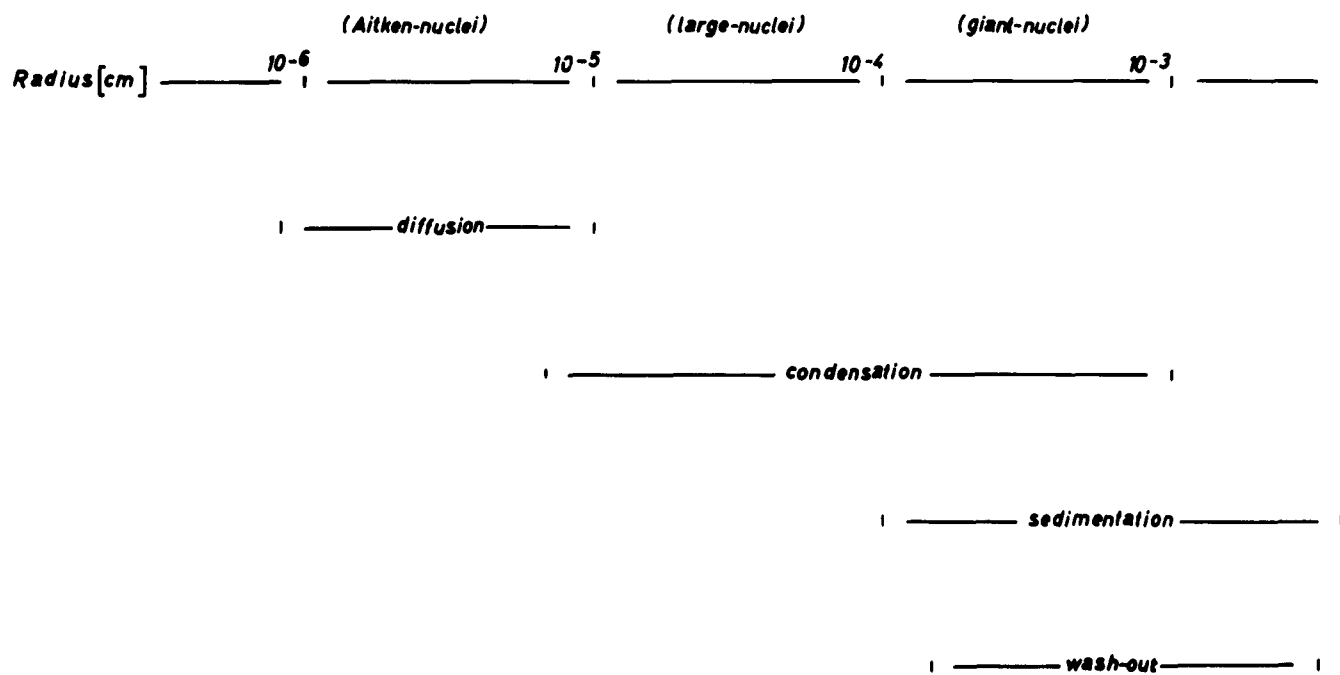


Fig.2

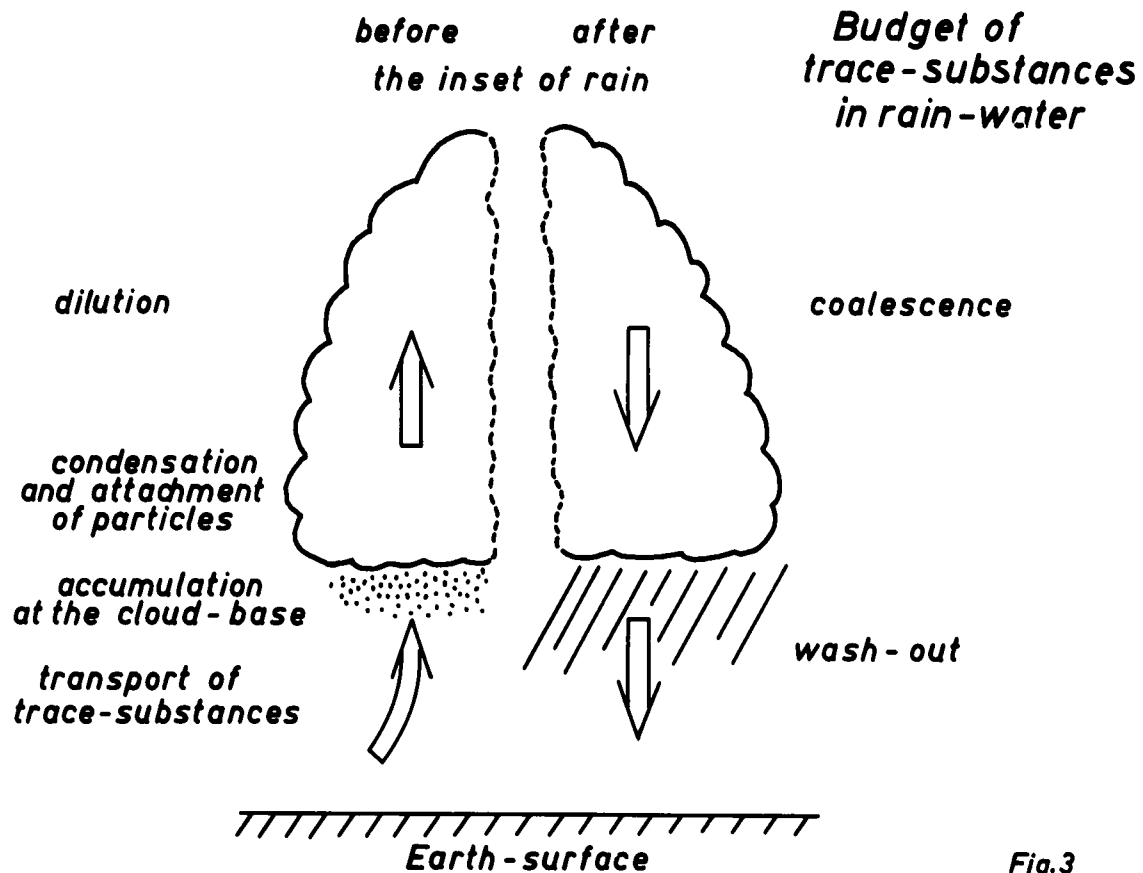
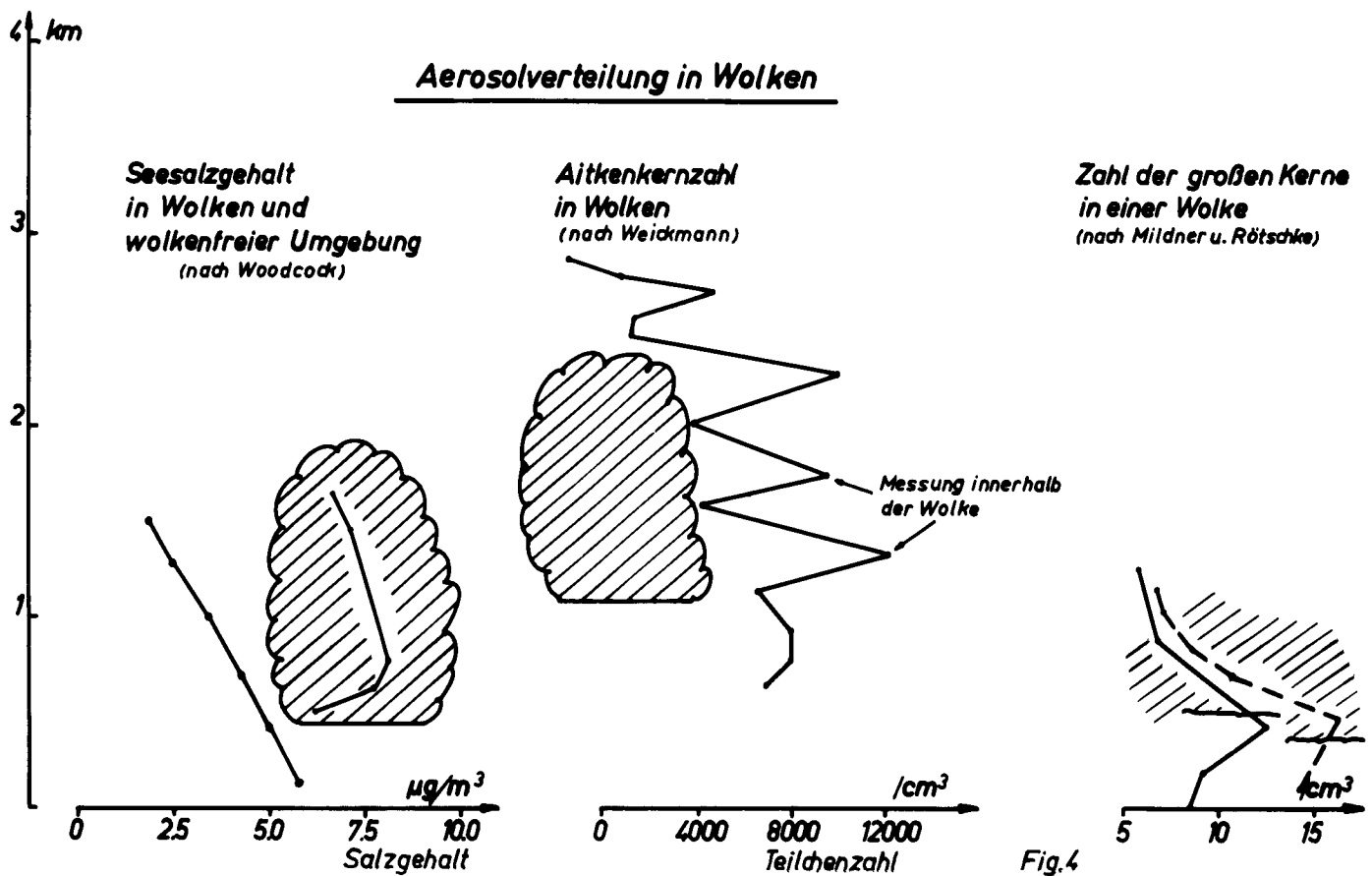


Fig.3



Verteilung von NH_3 in Gasphase, flüssiger u. fester Phase

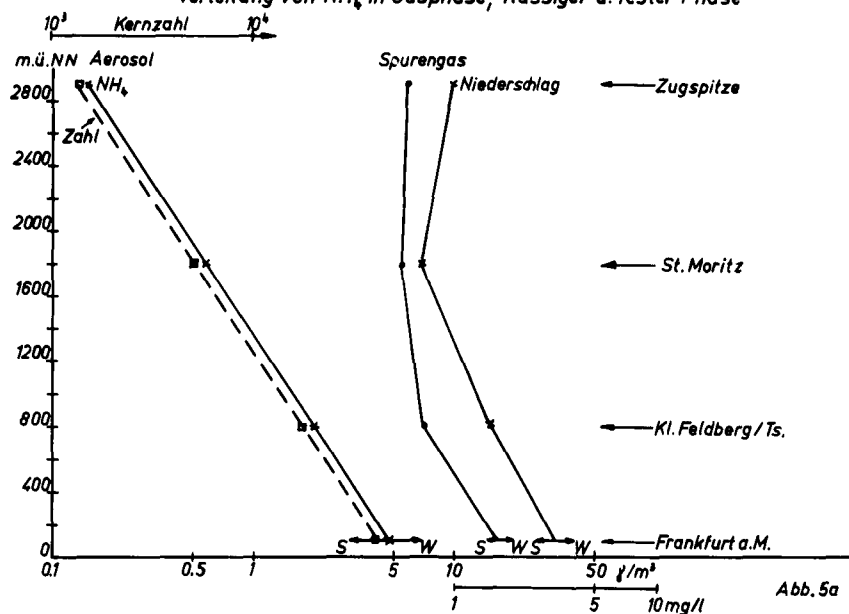


Abb. 5a

Verteilung der NO_3 -Konzentration in Gasphase, flüssiger u. fester Phase

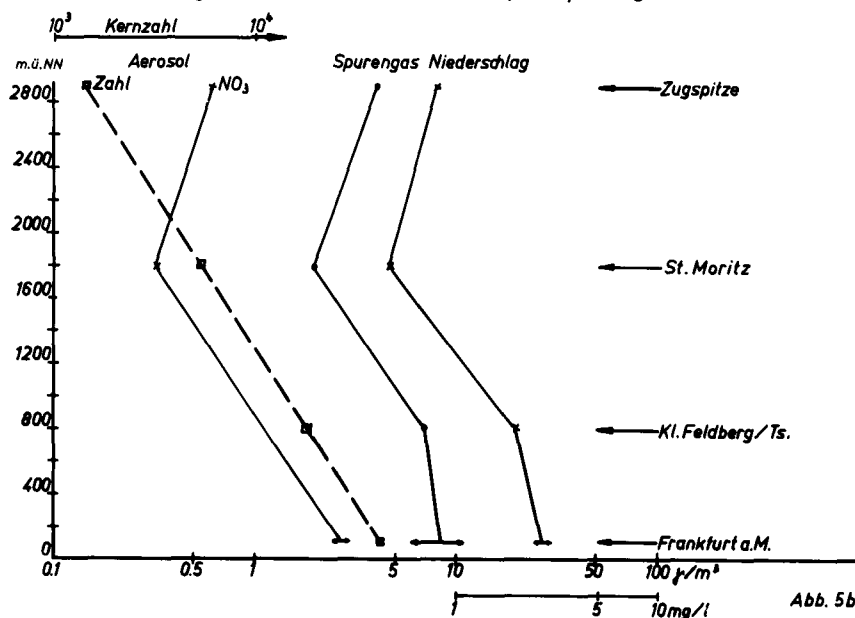


Abb. 5b

Regen (mg/l)
Spurengase ($\mu\text{g}/\text{m}^3$)

Verhältnis der Spurenstoffkonzentration im
Niederschlag zur Gaskomponente in der Atmosphäre

- 1 Frankfurt a.M.
- 2 Taunus-Observatorium
- 3 Zugspitze
- 4 Ultuna/Schweden
- 5 St. Moritz

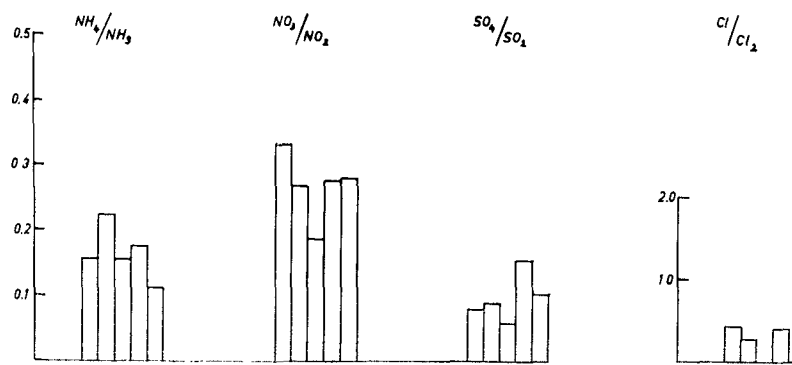


Fig. 6

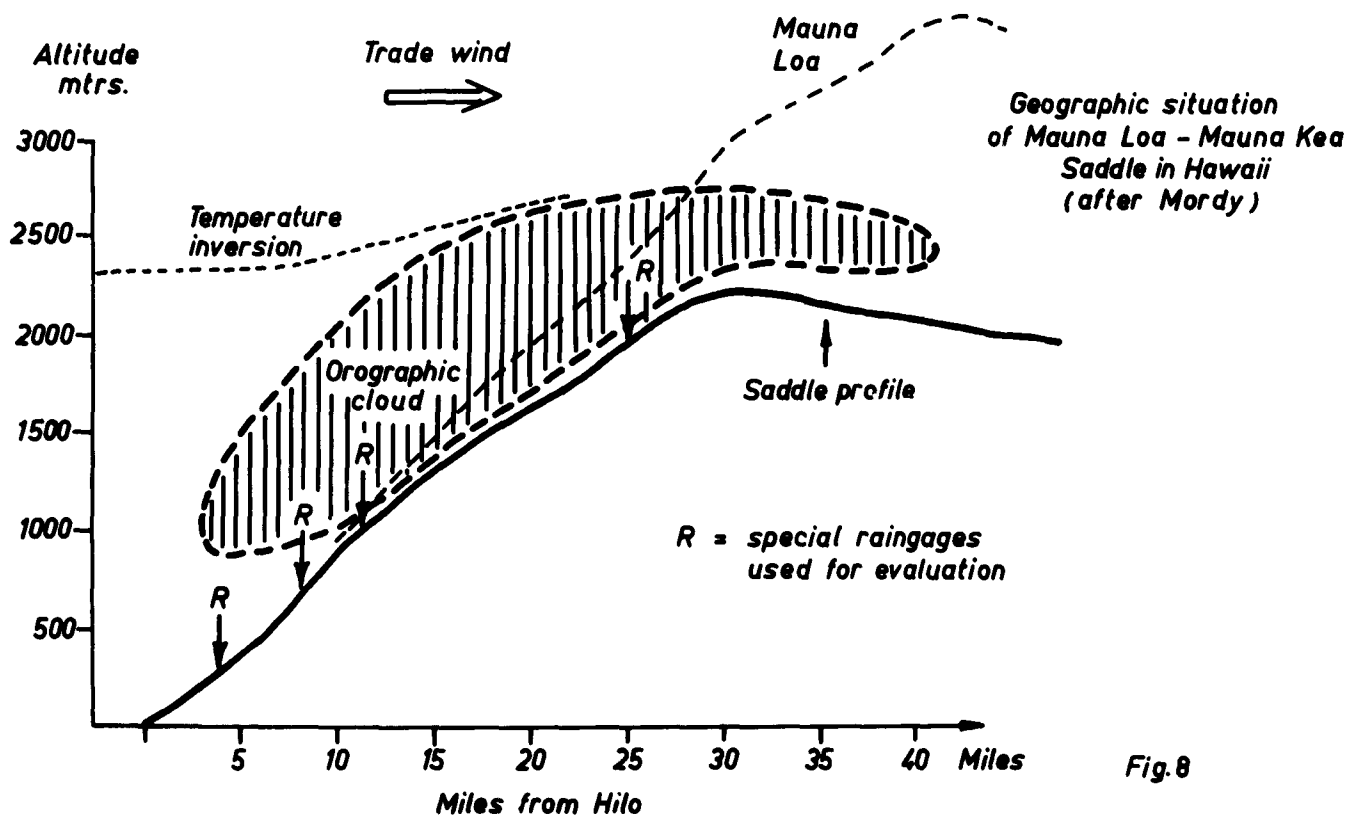
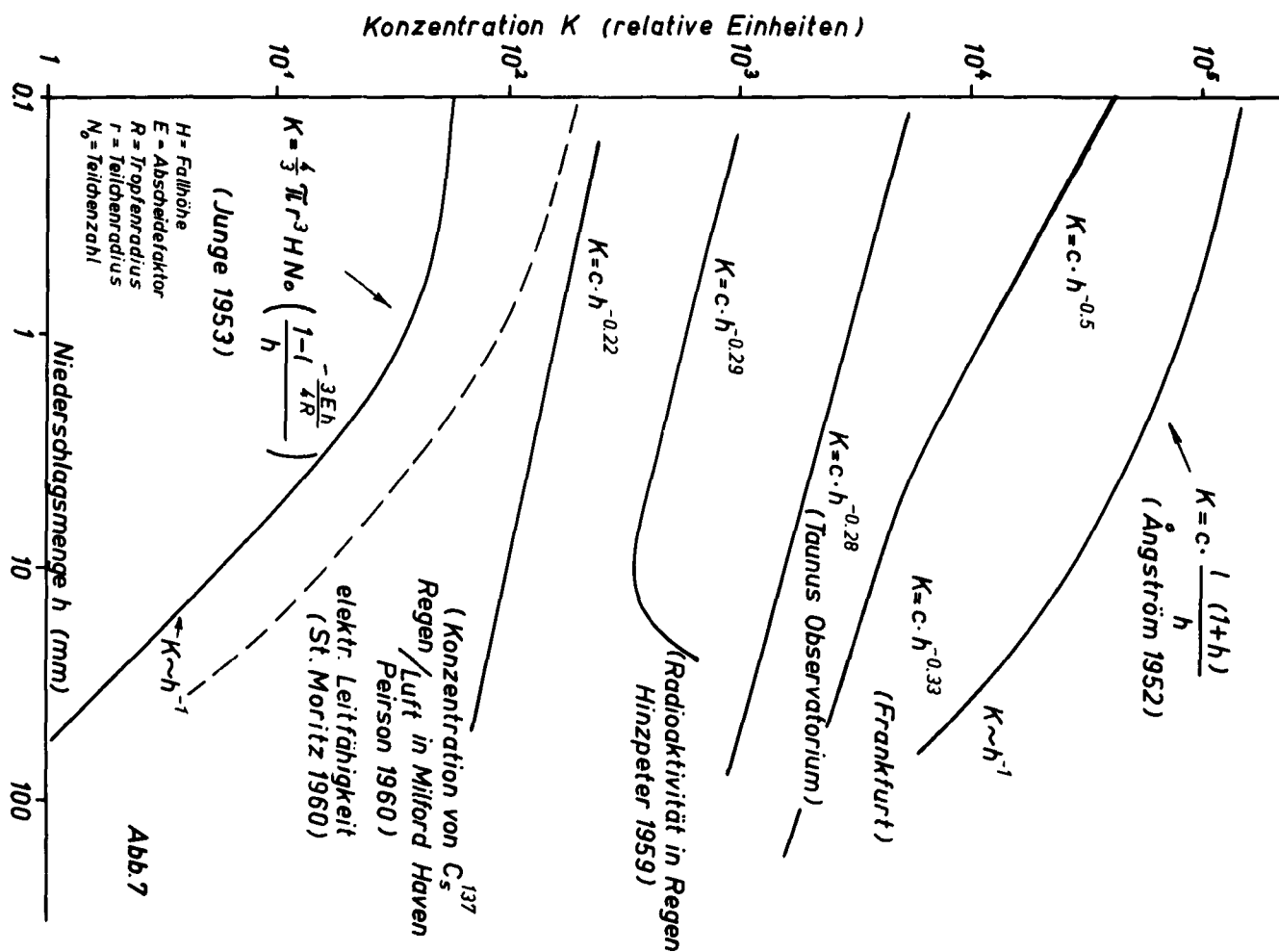


Fig. 8

*Evaluation of the chemical composition
of rainfall in Hawaii*

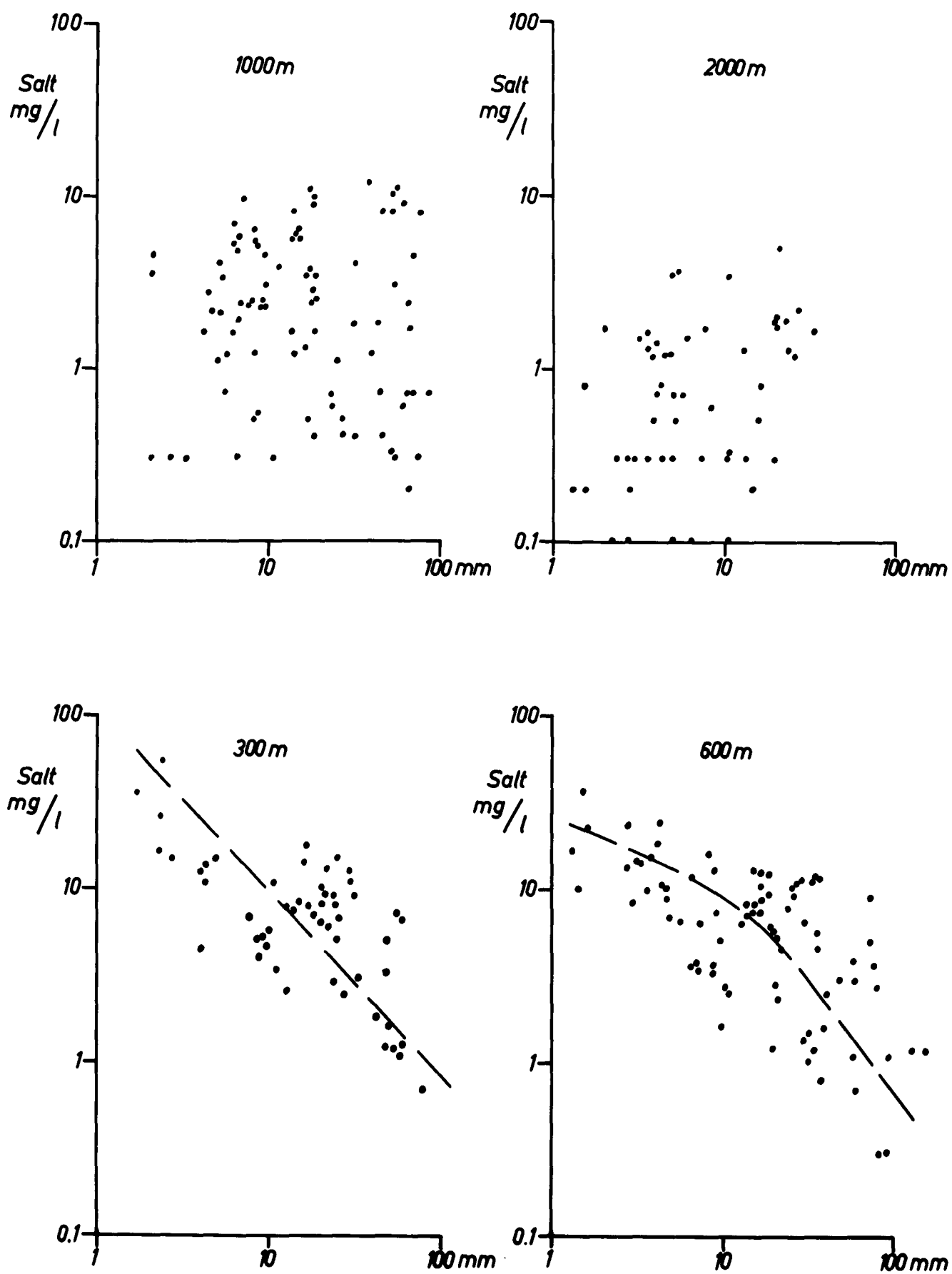


Fig. 9

Chemische Analyse von Einzelniederschlägen
Zugspitze April - Sept. 1961 (Probe 1-60)

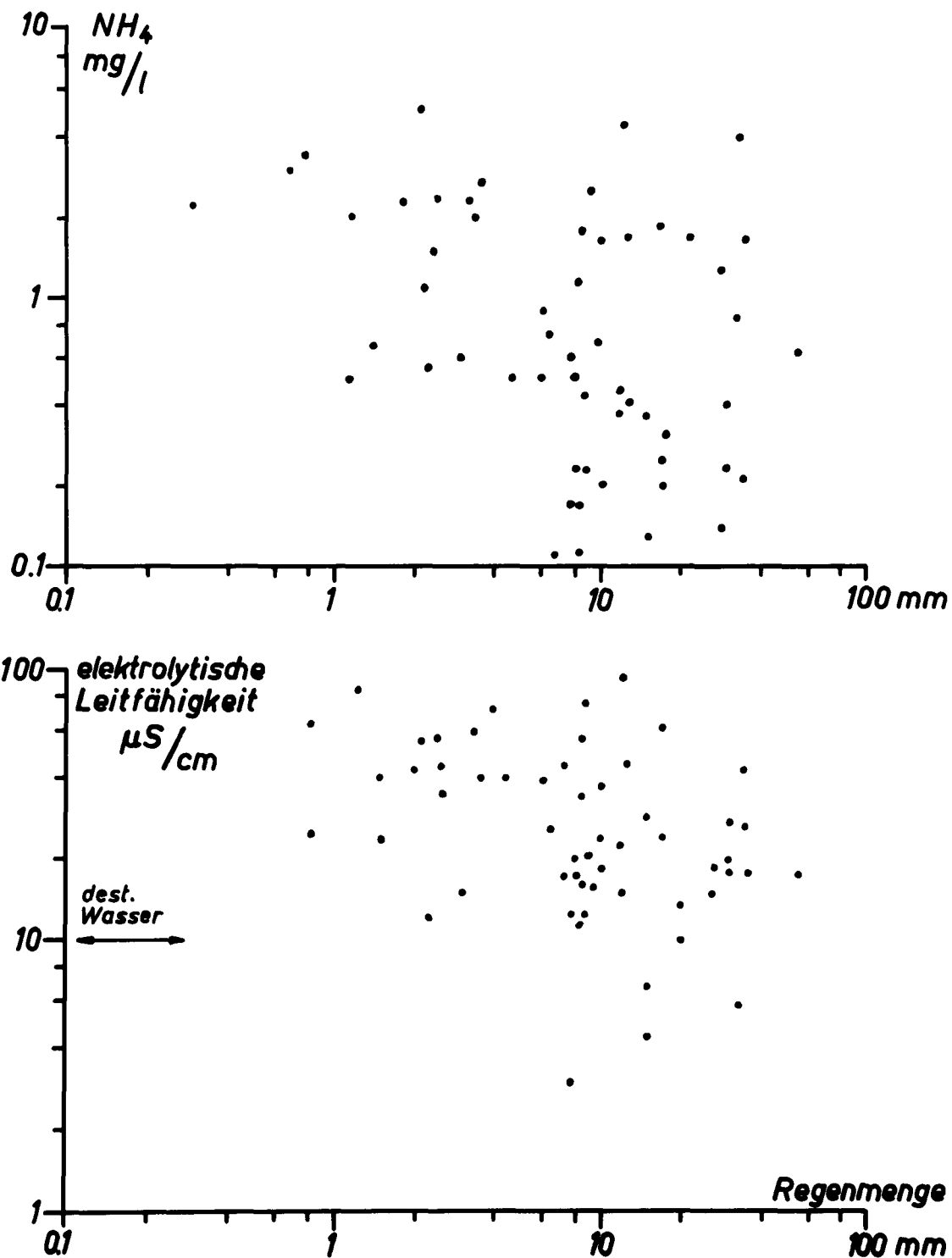


Fig. 10

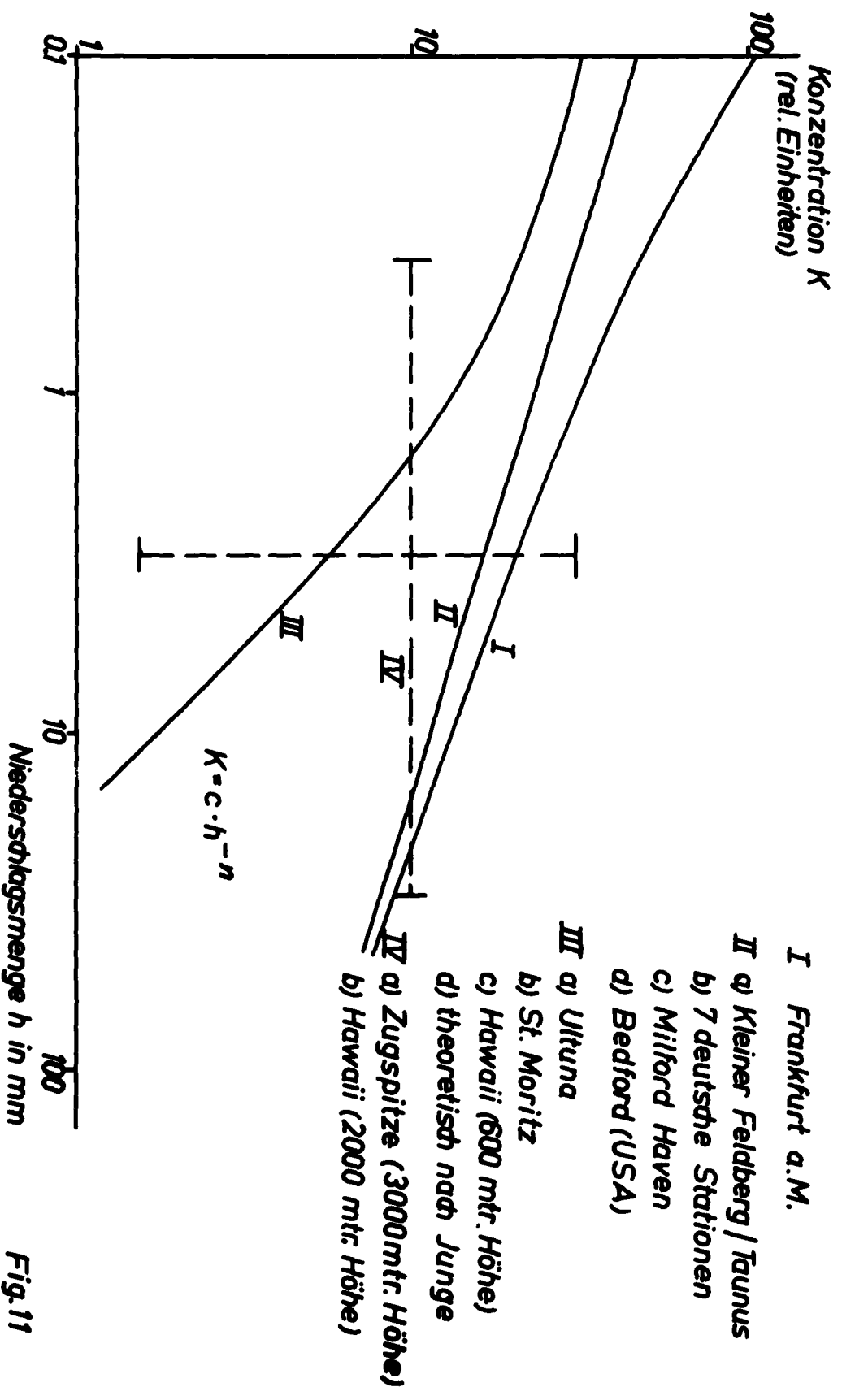
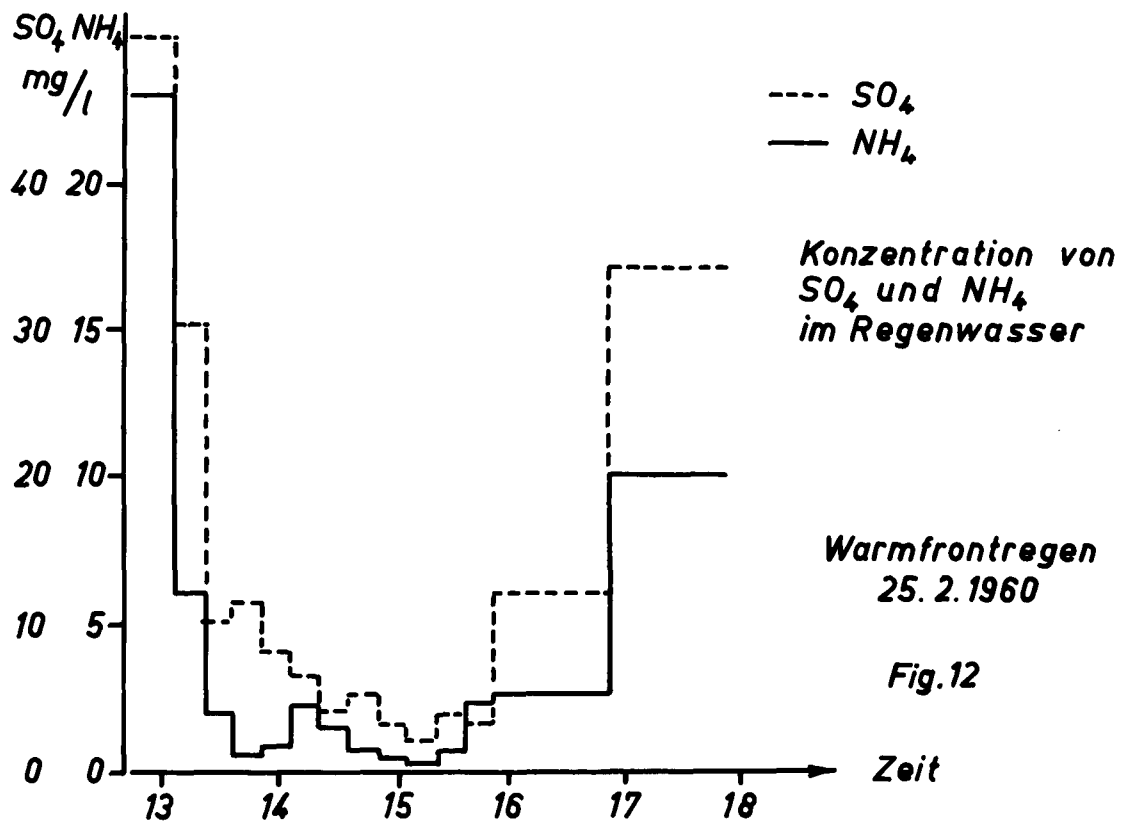
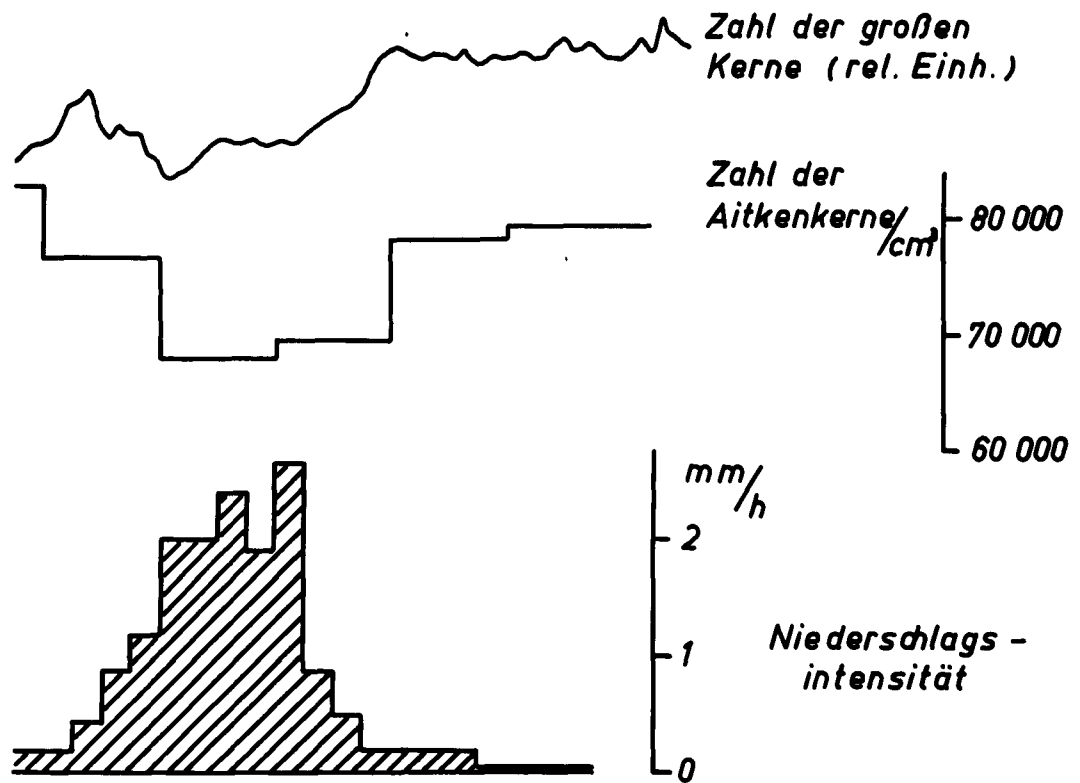


Fig. 11



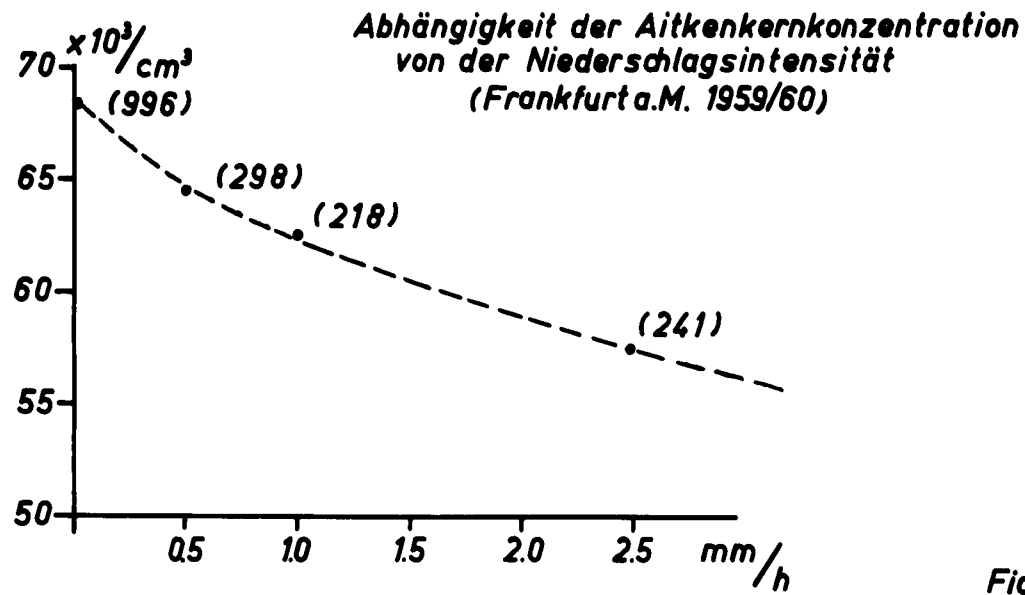
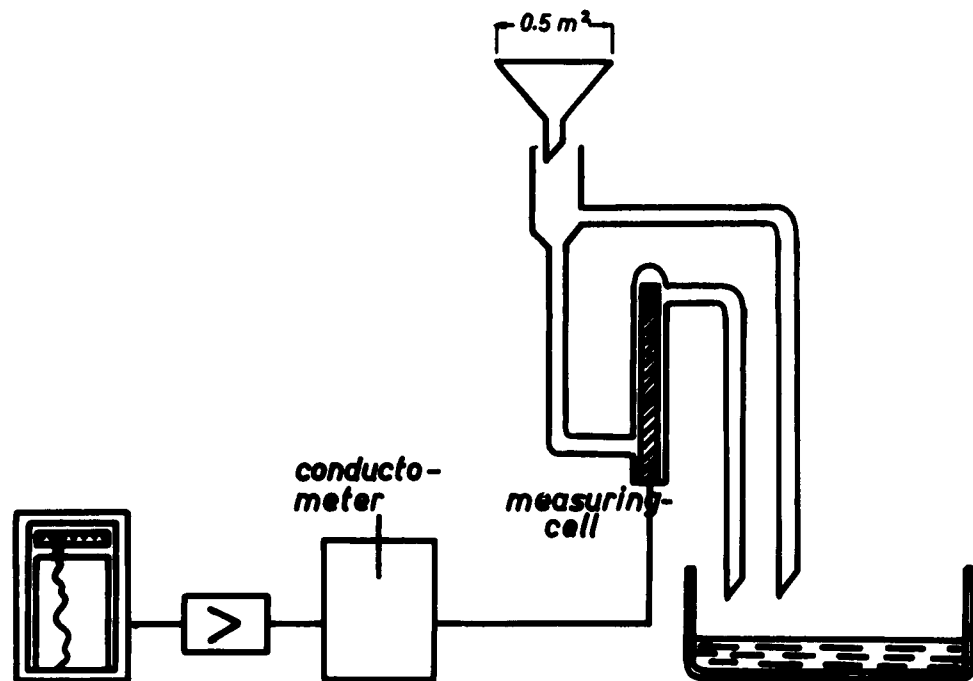
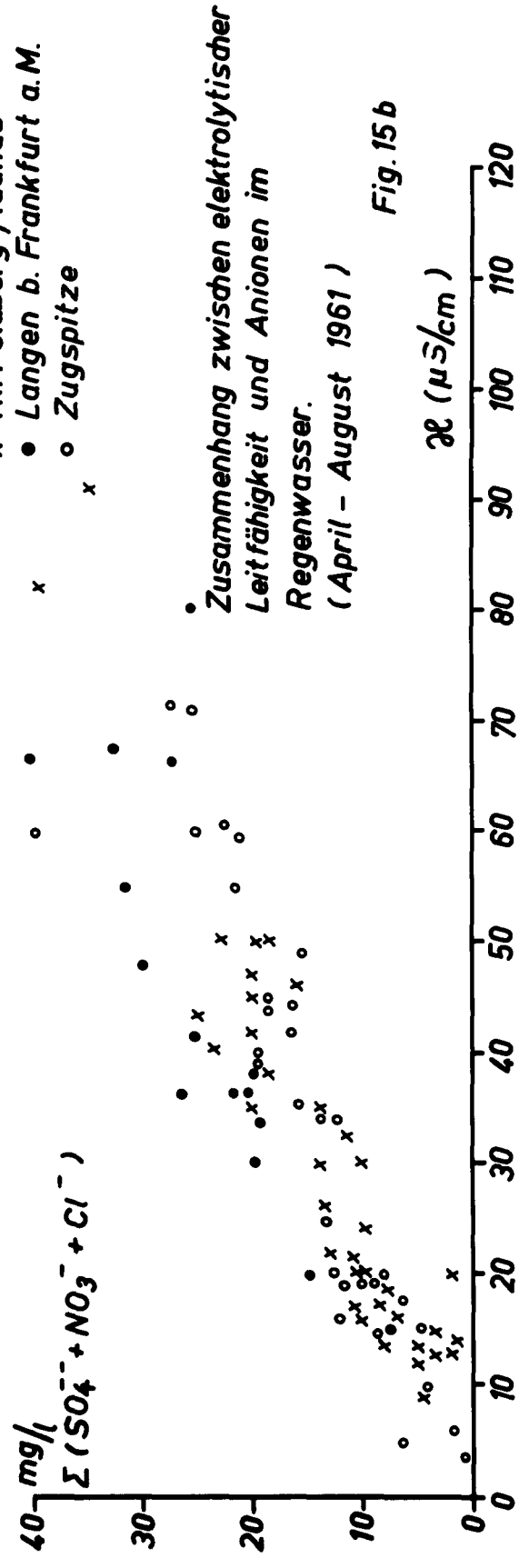
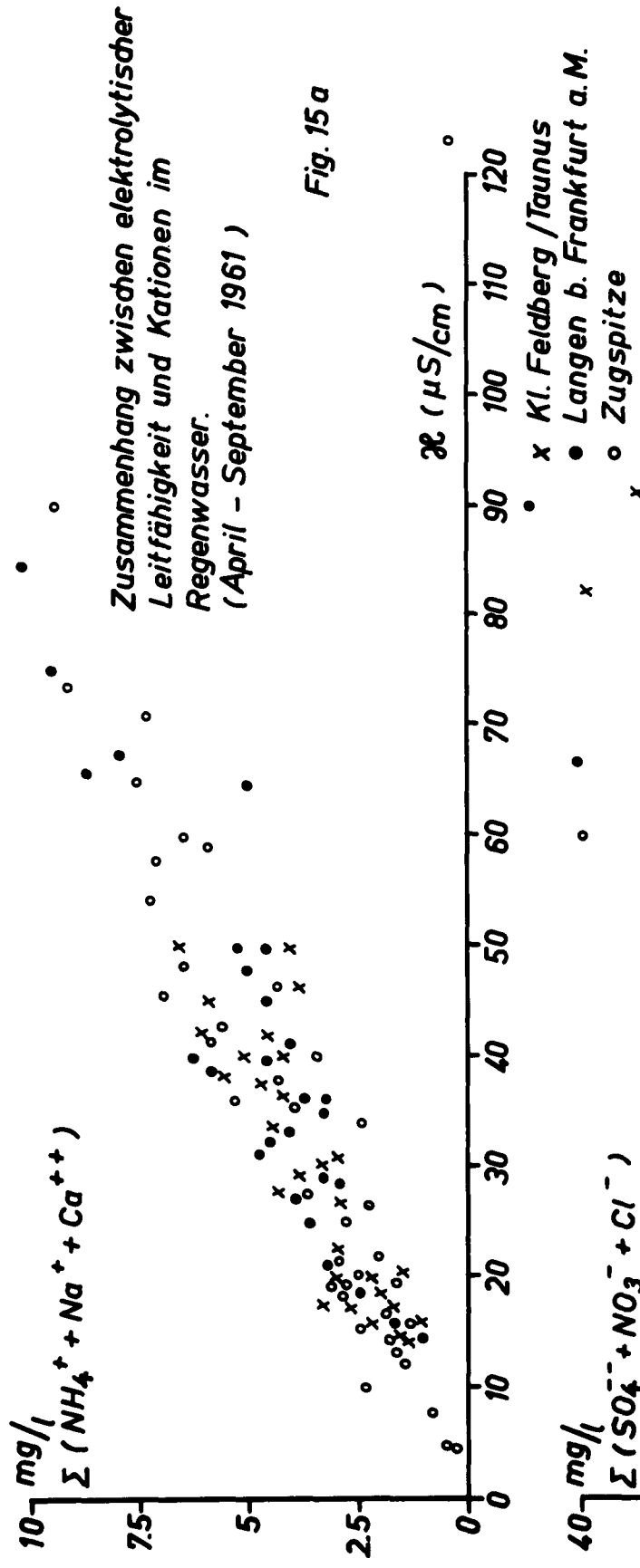


Fig.13



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

Fig.14



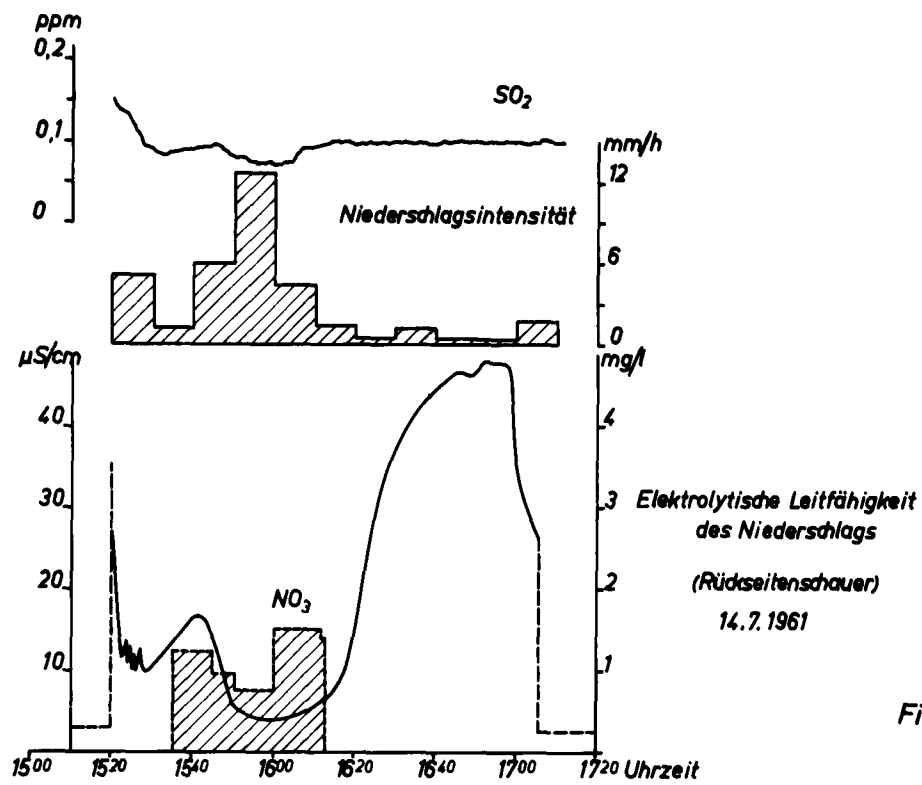


Fig. 16

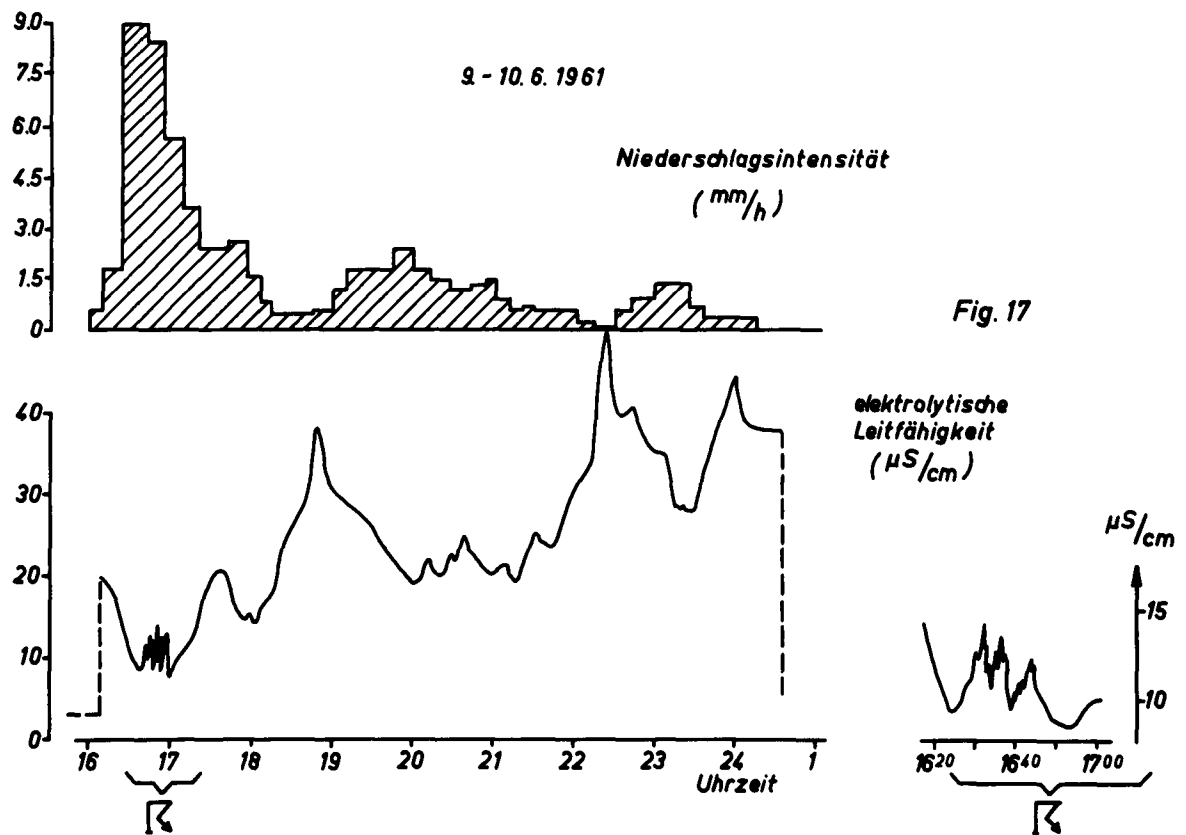


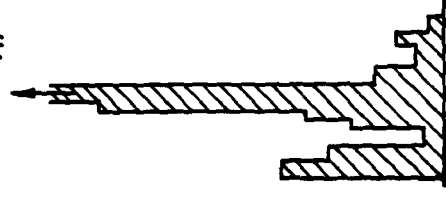
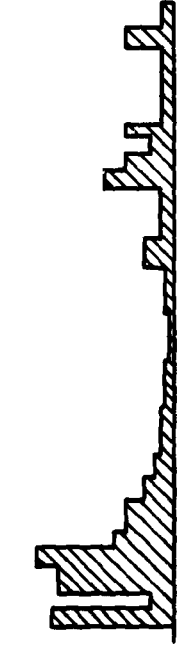
Fig. 17

7.5
6.0
4.5
3.0
1.5
0

mm/h

Niederschlags-
intensität

32 mm/h



(Einbruchgewitter)
27. 6. 1961

60
50
40
30
20
10
0

$\mu S/cm$

elektrolytische
Leitfähigkeit des
Niederschlags

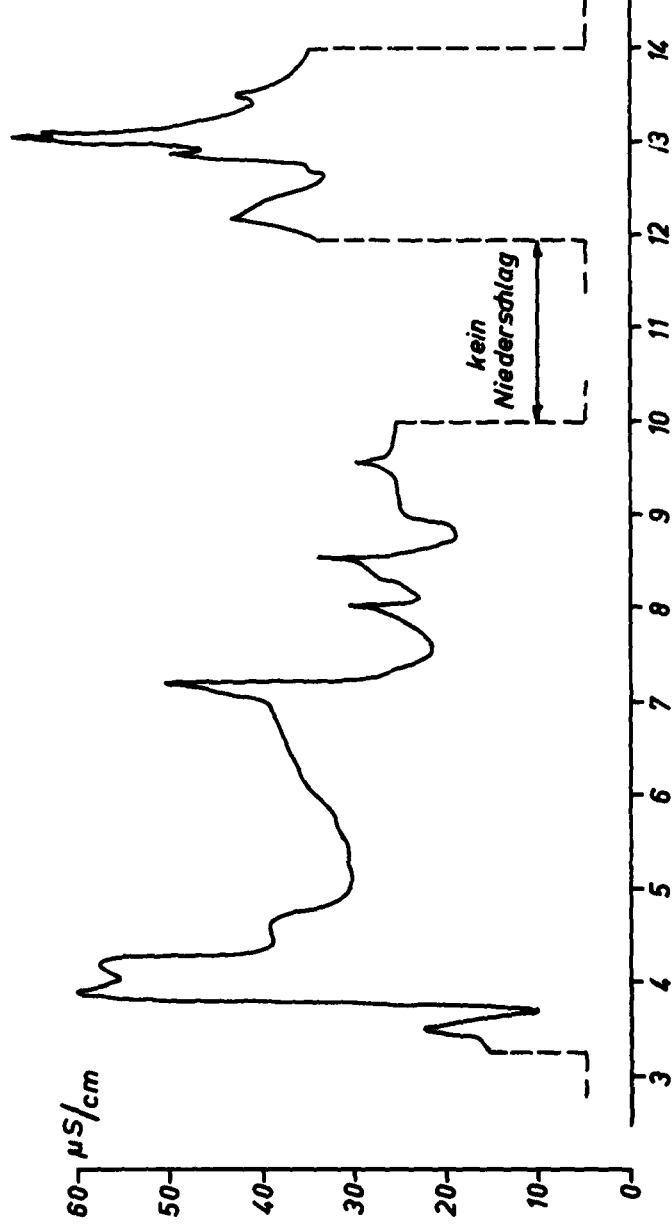
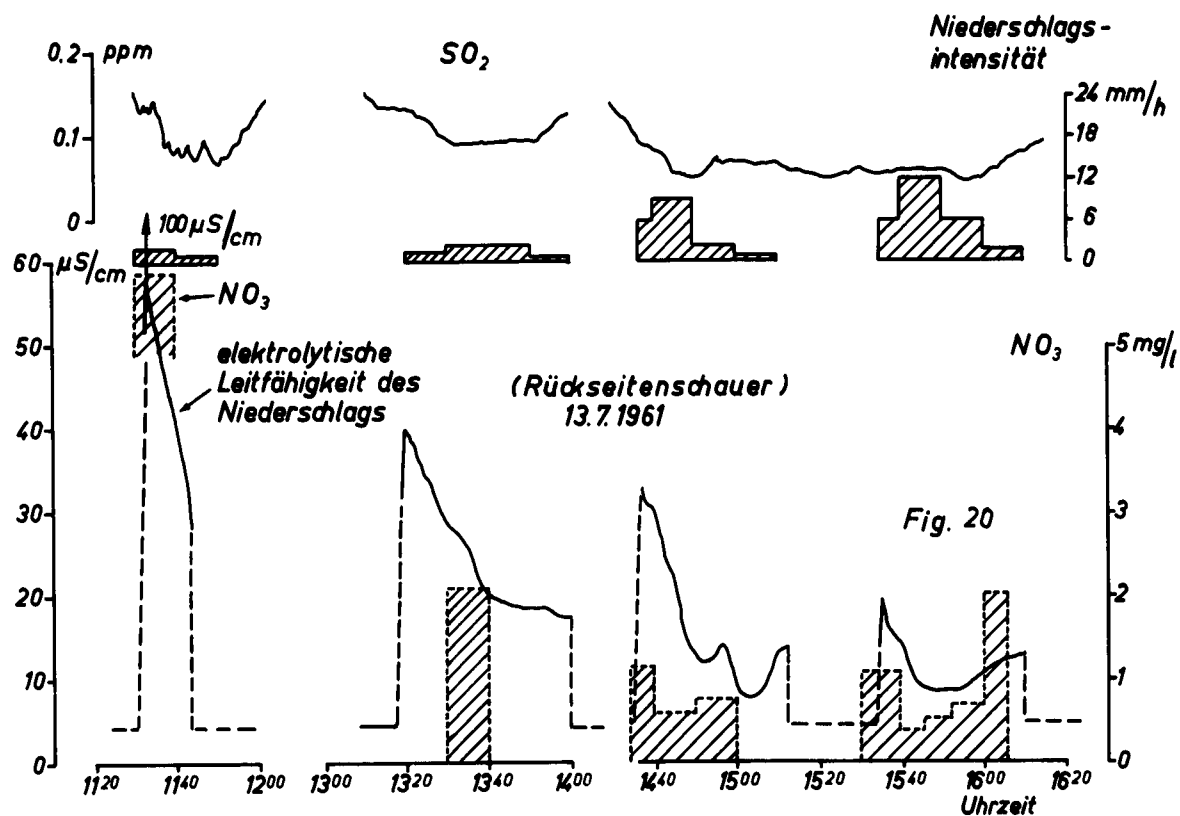


Fig. 18

Uhrzeit



0.2 0.5 1 2 5 10

$$\bar{K} = \frac{\sum K_i V_i}{\sum V_i}$$

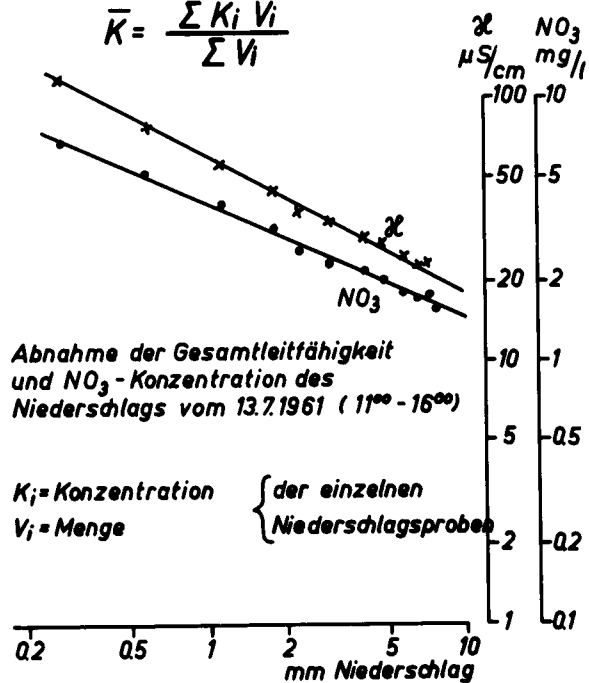


Fig. 19