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Part I

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Part II

Further Investigations on tropospheric wash-out.

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Part I

The concentration of chemical traces in glacier-ice

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Abstract

The report deals with the results of chemical analyses of melted ice-samples from an Austrian glacier and from an Arctic island. The concentration of the different components in the ice-samples from Austria is very low compared with the concentration of the same ions in freshly fallen precipitation. This discrepancy can most certainly be explained by the mechanism of the formation of glacier-grains. The series of ice-samples collected at the Arctic island covering the period 1920 to 1960 does not show any increase of the SO_4-concentration with time. The own results are finally compared with data gained by other authors.

Introduction

The concentration of trace-substances found in glacier-ice is primarily determined by the concentration of trace-material in precipitation as well as in the air-layer above the glacier-surface. Very few chemical analyses of glacier-ice were carried out up to now. E. Gorham (1, 2) reported on the chemical composition of glacier-ice sampled in Nordaustlandet Svalbord and in Northern Norway. A. Renaud (3) reported on the electrolytical conductivity of several samples from a Swiss glacier as well as on chemical analyses of the saline skin surrounding the glacier-grains. These investigations were carried out in connection with his theory of the transformation of snow into glacier-ice.

C.E. Junge (4) assumed that the trace-substances in Greenland-ice are conserved over long periods, because the low average temperature of the air prevents melting. He therefore carried out chemical analyses of ice-samples collected at site II in Greenland (about 200 miles east of Thule at an altitude of 2500 mtrs.). These ice-samples covered the period from 1915 to 1957. Junge had the idea that samples from the earlier period of this century might have a lower SO_4-concentration than samples from more recent times. An increase of the SO_4-concentration of glacier-ice is considered to be caused by the appreciable increase of anthropogeneous and industrial SO_2-emission into the atmosphere in temperate latitudes of the northern hemisphere. The results of the investigations by Junge revealed, that the SO_4-concentration of glacier-ice is higher by an order of magnitude compared with the concentration of the other components. He could however not find an increase of the SO_4-concentration during the period covered by the ice-samples. No continuous increase of the SO_4-concentration of the ice-samples could be detected during the period 1915 to 1957.

Investigations on the Hintereisferner (Austrian Alps)

The results gained by Junge might have been influenced by the fact that the residence time of man-made sulfur in the atmosphere is relatively short. This means that wash-out by precipitation may remove the major part of industrially produced SO_2 before the air-masses carrying the industrial emissions arrive in Greenland. In order to exclude this possibility we have analyzed ice-samples from an alpine glacier. In cooperation with Professor Hoinkes from the University of Innsbruck who has a great experience and knowledge of the structure of the Hintereisferner in Tyrolia, ice-samples were collected on that glacier. The central location of the alpine glaciers in Europe ascertains that air-masses travelling over the industrial areas reach the Alps within a few days.

An exact determination of the age of the ice-samples collected was not possible. For a first survey we tried to receive samples of very different age. By his profound knowledge of that particular glacier Professor Hoinkes was able to give the approximate period of formation of each of the analyzed samples.

We analyzed six samples from each of the four different periods of time available. The following table shows the average values of the concentration of the different components analyzed:

Approximate Age of sample	SO_4	NO_3	NH_4	Cl	Na	Electrol. conductivity µS/cm	pH
		(mg/ltr.)					
several hundred years	0.050	0.020	0.030	0.40	0.25	2.3	5.2
approx. hundred years	0.048	0.020	0.032	0.44	0.27	2.5	5.2
less than hundred years	0.050	0.022	0.044	0.46	0.33	2.8	5.0
several years	0.077	0.022	0.046	0.55	0.41	5.2	5.0

Discussion of results

The most surprising result of the analyses is the high grade of purity. The electrolytical conductivity of the samples was in the range 2 to 5 /u S/cm comparable with distilled water. Although no analyses of freshly fallen snow were carried out on Hintereisferner yet, its constitution would be probably comparable with the trace-substance concentration of snow on Zugspitze (2960 m) and at St. Moritz (1800 m). At these two stations chemical analyses of precipitation were carried out during longer periods by the authors of this report (5). The concentration of trace-substances in precipitation at these two locations is five to ten times higher than in the ice-samples from Hintereisferner as shown in the table below:

Site of measurement	SO_4	NO_3 (mg/l)	NH_4	Cl	electrolytical conductivity /uS/cm
Zugspitze	1.0	0.8	2.8	1.6	-
St. Moritz	0.4	0.8	1.2	-	36

The ice-samples from more recent periods have a higher SO_4-concentration compared with samples from older periods. It seems however doubtful whether this increase of SO_4 in the ice is caused by the increase of atmospheric SO_2-concentration in the atmosphere of the Northern hemisphere. Besides of the increase of the SO_4-concentration we also found an increase of the electrolytical conductivity of the ice-samples indicating an increasing content of soluble salts in the glacier ice concerned. The Chloride- and Sodium concentration of the samples was higher than that of every other of the analyzed components. The ratio Na/Cl fluctuates in the range from 1/1.6 and 1/1.3 and shows therefore good agreement with Junges results who found an average Na/Cl ratio of 1/1.3. This value deviates from the Na/Cl ratio of ocean water which is somewhat higher reaching values of 1/1.8.

An explanation for the great purity of glacier-ice and the obvious discrepancy between the concentration of trace-substances in freshly fallen snow and the concentration of the same traces in glacier-ice must be sought in the mechanism of the formation of the glacier-grains. The growth of the glacier-grains during the conversion of the firn into solid ice has been described by G. Tamann (6) and A. Renaud (7). During this conversion-process a separation of the salt-solution from pure water takes place. The glacier-grains grow to a size-ranging from 1 cm to 15 cm diameter while the liquid saline layer surrounding the glacier-grains has a thickness of only about 1/10 of the diameter of the ice-grains. The presence of salts is therefore limited to the outer layer of the grain. The salt-concentration decreases from the surface towards the center of the glacier-grains. It can be expected that in the case of a glacier in temperate latitudes where melting occurs during the summer-months, the saline solution is carried away with the meltihg water. Our investigations carried out on Hintereisferner permit therefore important conclusions on the interior structure of the glacier-ice and possibly on the formation of glacier-grains.

Analysis of ice-samples from Axel Heibergland (Arctic)

After the conclusion of the analyses of ice-samples from Hintereisferner we were supplied with a number of ice-samples from the arctic island Axel Heibergland. In this connection we are very grateful for the kind assistance given by the Air Force Cambridge Research Laboratories, Office of Aerospace Research, Bedford (Mass.). The samples were collected by the Jacobsen-McGill Arctic Research Expedition during summer 1961 and a detailed stratigraphy with age-determination of the samples was carried out by Dr. F. Müller and his collaborators. The samples covered the period from 1920 to 1960. According to assumptions by R. Revelle and H. Suess (8) the world **fuel**-consumption increased during that period from 12.8×10^8 tons to 25×10^8 tons. The ice-samples were collected in a shaft which was dug with a slope of 41°, an average diameter of 2 mtrs and a total length of 27.2 mtrs in approx. 6600 feet altitude. The geographical coordinates of the site are 79°47'N and 92°20'W.

The results of the analyses of the different chemical components are entered in Figs. 1, 2 and 3 in dependance of the age of the ice-samples. The Na-analyses are incomplete since the amount of melting-water at our disposal was insufficient in some cases. The samples from 1924 were obviously contaminated. This is indicated by the high SO_4- and Cl-concentration and the high value of the electrolytical conductivity. The fluctuation of the concentration of the different components is partially caused by differences in the annual amount of precipitation. Unfortunately we had no samples of freshly fallen snow from Axel Heibergland which would have permitted a comparison with the trace-substances concentration in ice.

The NO_3-concentration shows a slight increase, while the electrolytical conductivity as well as the NH_4-concentration decreases slightly after 1940. The SO_4-concentration remains constant during the 40 years-period. With the exception of two samples the concentration of sodium is always lower than the concentration of chloride. During periods of considerable length a parallel trend between sodium- and chloride-concentration can be stated.

Comparison with the research of other investigators

It is of great interest to compare our results with the few data on chemical analysis of ice-samples which have been published by other authors up to now. The following summary shows a good agreement of the different analyses as far as the order of magnitude of the concentration is concerned. A considerable higher concentration was found by Gorham. His samples were however taken from the surface of the glacier or in a crevasse where it is difficult to prevent the contamination by melting water or wind-driven dust.

Site of collection (Author)	SO_4	NO_3 (mg/l)	NH_4	Cl	Na	K	Ca	electr. conduct. (µS/cm)	pH
Spitzbergen (Gorham)	0.8	-	-	3.2	2.0	0.2	0.38	-	6.2
Norway (Gorham)	-	0.01	0.013	-	0.5	0.03	-	1.8	5.8
Greenland (Junge)	0.25	-	-	0.037	0.03	0.01	0.035	-	-
Switzerland (Renaud)	-	-	-	-	-	-	-	1-37	-
Austria (Georgii)	0.057	0.021	0.038	0.43	0.31	-	-	3.3	5.2
Axel Heibergland (Georgii)	0.028	0.013	0.029	0.07	0.05	-	0.07	1.9	5.2

The figures of our analyses show that an increase of the atmospheric SO_2-concentration on the northern hemisphere since the beginning of the industrial age does not result in a measurable increase of the SO_4-concentration of glacier-ice. A detection of such an increase seems also very difficult owing to the separation of saline solution and pure ice-crystals during the formation of the glacier-grains. In contrast to the assumption of an increase of the SO_4-concentration in glacier-ice we find that the SO_4-concentration of the ice of the Austrian Hintereisferner is very low compared with the SO_4-concentration in precipitation in the alpine region. Higher SO_4-concentrations can be expected in the thin saline layer between the ice-grains. A. Renaud (3) found in this layer SO_4-concentrations ranging up to 5 mg/ltr. Our investigations do not permit yet a concluding decision on the distribution of trace-substances in glacier-ice. Additional studies must be extended to chemical analyses of the firn-layer and the melting-water of the glacier. It is hoped that they will provide a better understanding of the mechanism of the transformation of firn into glacier-grains.

The authors would like to express their gratitude to Professor Dr. H. Hoinkes, University of Innsbruck and his collaborators for valuable assistance during the performance of this investigation.

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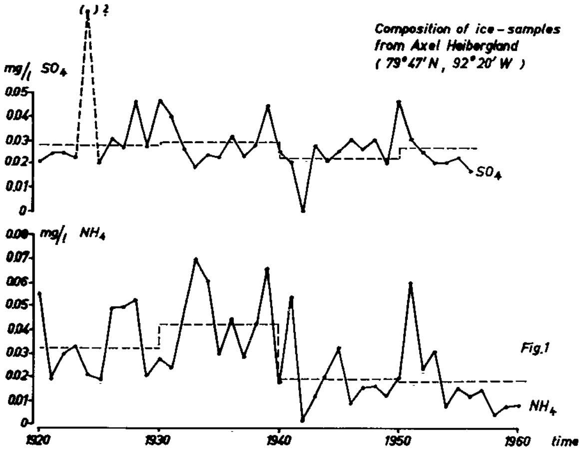
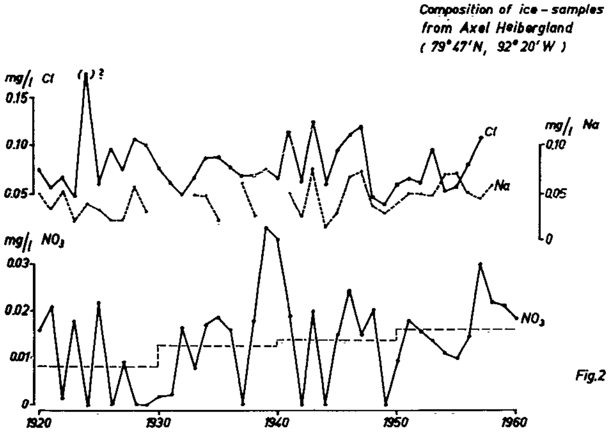


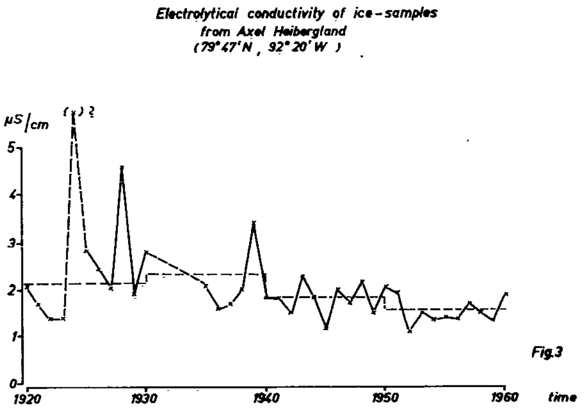
Composition of ice-samples from Axel Heibergland (79°47'N, 92°20'W)

Fig.1



Composition of ice-samples from Axel Heibergland (79°47'N, 92°20'W)

Fig.2



Electrolytical conductivity of ice-samples from Axel Heibergland (79°47'N, 92°20'W)

Fig.3

Part II

Further investigations on tropospheric wash-out

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Abstract

The following report summarizes recent research on the budget of trace-substances in cloud- and rainwater conducted at three sampling-stations in different altitudes. Further results on the importance of gaseous traces for precipitation-chemistry as well as on simultaneous records of total concentration of trace-substances, pH-value and radioactivity during individual rainfalls are communicated.

Introduction

The mechanism of incorporation of trace-substances into cloud- and raindrops is very complicated and complex. Several different processes contribute to the concentration of trace-substances in cloud- and in rain-water and one major aim of our investigations is to separate these distinct processes by experimental techniques endeavouring by this a better solution of the whole process. The following problems are being dealt with separately:

1) What is the contribution of gaseous traces and of aerosol-particles to the total trace-substance concentration in precipitation measured at ground level?

2) What is the contribution of "rain-out", i.e. the processes taking place within the cloud and of "wash-put", i.e. the contribution of processes taking place during the fall of rain-drops below the cloud-base to the total trace-substance concentration in precipitation?

3) How important is the process of partial evaporation of rain-drops during their fall through the cloud-free zone below the cloud base?

In our previous report (1) we have laid down that a complete theoretical treatment of the wash-out mechanism is impossible that theoretical solutions have only been found for the consumption of aerosol-particles by condensation and by impaction during the fall of rain-drops below the clouds (wash-out). In a recent paper Goldsmith, Delafield and Cox (2) investigated the so-called "Facy-effect". This is the name for the phenomenon by which aerosol-particles near cloud-droplets are being moved by the diffusion current of water molecules towards a condensing droplet. Facy (3) suggested that particulate matter near growing droplets may be scavenged from the atmosphere. The above named authors were able to show that the absolute efficiency of this diffusion-process in scavenging aerosol-particles from the atmosphere during the growth of cloud-drops is very low. The wash-out due to this effect is less than one percent of the total observed wash-out for each condensation-cycle occuring in nature.

Generally it can be expected that the ground-level concentration of precipitation is proportional to the concentration of gaseous and particulate trace-substances in the atmosphere under consideration of different absorption-coefficients and inversely proportional to the liquid water available which depends of a number of cloud-physical parameters.

This can expressed in the following formula

$$K_1 = \frac{\varepsilon \cdot c}{l}$$

c = concentration in $\mu g/m^3$
ε = coefficient of absorption = f(r)
l = liquid water content

ε comprises condensation + diffusion + Brownian motion

In addition to these processes impaction of particles and evaporation of water have to be taken into account

$$K = f\ (K_1 + K_2)$$

$f \geq 1$ = effect of evaporation
K_2 = impaction = f(r).

It needs no special mention that with respect to trace-gases only those are of interest which are soluble and react chemically with other components in the drops leading to irreversibel compounds. This transformation process from the gas-phase to the liquid phase resp. after evaporation of the drops solid phase has only be investigated for the important system ammonia-sulfur dioxide-water (4).

It can be expected that the absorption-coefficient for gases is smaller than for aerosols. On the other hand the concentration of gases available is larger than of the same components in solid state as has been laid down in details in Annual Report No 2.

The budget of trace-substances in precipitation

During the recent months chemical analyses of cloud-water and 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 Fig. 1 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 raingauge. Instruments of this type have been successfully used by Grunow (5).

A summary of the results of chemical analyses in non-precipitating and in precipitating clouds shows Fig. 2. Here we have entered the average values of the electrolytical conductivity of cloud- and rainwater collectedat the three different sampling-stations. The electrolytical conductivity represents a true picture of the total concentration of soluble inorganic components in the samples. The existing close correlation between chemical components in rain and electrolytical conductivity was demonstrated in Annual Report No 2.

As can be seen in Fig. 2 the concentration of trace-substances in cloud-water is very high near the cloud-base. The high values of electrolatical conductivity near the cloud-base can be explained by 1) the supply of trace-substances from the ground which are carried upwards and are collected by the cloud-droplets near the condensation-level, and 2) by the low liquid-water content of the cloud near condensation-level.

With increasing altitude within the cloud we find 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 amount of liquid water set free by condensation with increasing altitude.

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 a further 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. 2 permits the conclusion that approximately 2/3 of the trace-substance concentration in rain-water at ground-level has been incorporated within the clouds and 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 3 mms.

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. This is demonstrated for Zugspitze (upper part of Fig. 3) and for Kl. Feldberg/Taunus (lower part of Fig. 3). On the Zugspitze the concentration of NH_4 and NO_3 is slightly higher in cloud-water (W) than in precipitation (N), while the SO_4-concentration is higher in precipitation than in cloud-water. The electrolytical conductivity ($\mathcal{K}$) summarizing the different compounds is equal in cloud-water and precipitation on the Zugspitze. The dashed line indicates the base-concentration applied for the Feldberg-diagram. On Kl. Feldberg the concentration of all components analyzed is much higher in cloud-water than in precipitation. The greatest difference is found between the concentration of SO_4 in cloudwater and precipitation. In this case the ratio is 1 : 10. This ratio is a further proof for the importance of the cloud-drops as collectors for trace-substances carried upward from the polluted ground-layer of the atmosphere into the region of cloud-formation. The SO_4-concentration of precipitation does not show much difference between 3000 mtrs. and 800 mtrs. altitude. The same applies to the electrolytical conductivity of precipitation as stated above.

The incorporation of gaseous traces into cloud- and precipitation elements

In our Annual Report No 2 as well as in a paper by H.W. Georgii (6) the importance of the absorption of gaseous traces by cloud- and raindrops for rain-chemistry was stressed. It is still very difficult to give any quantitative data on the amount of trace-substance found in rainwater which can be attributed to gas-absorption since no measurements of the concentration of the gases concerned in the free atmosphere have been made yet. First attempts to measure SO_2 and NO_2 by aircraft ascents up to altitudes of about 3500 mtrs. have been made during fall 1962. The evaluation of the data is still under way.

Recent laboratory tests support the assumption on the absorption of trace-gases in rainwater. In the course of these studies atmospheric air was at first passed through a filter to free it from its content of natural aerosol-particles and then led continuously at a low flow-rate of 10 cm^3/sec over the slightly stirred surface of rainwater or doubly distilled water kept in a closed basin. The apparative set-up is demonstrated in Fig. 4. The surface of the rainwater contained in the closed glass-basin is moved by bubbling pure nitrogen through the water. Nitrogen does not react in any way with the rainwater or distilled water. These studies show that soluble trace-gases contained in atmospheric air are readily absorbed by the rain-water in the basin. Fig. 5 shows the results of several test-runs with respect to the incorporation of nitrogen-dioxide in rainwater resp. destilled water. The concentration of NO_3 and NO_2 in the water-sample was checked daily. Each test-run was extended over a period of a fortnight. The curves (upper curves for rainwater, lower curves for distilled water) show that atmospheric NO_2 is readily taken up. After the passage of 20 m^3 outside air (at the given flow-rate) the NO_3-concentration in rainwater increased from an initial concentration of 0.18 mg/l to 0.45 mg/l at the end of the experiment. In contrast to NO_3, the

NO_2-concentration changes only very little from 0.04 mg/l to 0.08 mg/l showing that the subsequent oxidation from NO_2 to NO_3 after absorption is a rather swift process. A similar result was obtained for distilled water. In this case the NO_3-concentration increased from zero to 0.35 mg/l after the passage of 20 m^3 outside air. The NO_2-concentration increases from zero to approximately 0.08 mg/l after the passage of 8 m^3 air and remains constant at this concentration. Obviously the balance between the absorption of atmospheric NO_2 and the oxidation to NO_3 is reached. This result is in agreement with data quoted by Eriksson (7) on the nitrate-concentration in rain indicating that the nitrite-concentration is roughly 10 percent of the nitrate-content in precipitation. In order to obtain reliable data it is important that the NO_2-analysis of the rain-water sample is completed very soon after collection. Comparison between the results gained during winter 1961/62 and those of test-runs carried out during summer 1962 show that the NO_3-concentration in the rain-water is related to the outside atmospheric NO_2-concentration. This is indicated by the two curves valid for winter and summer and the two columns on the right side in the lower part of Fig. 5. The average atmospheric NO_2-concentration during January and February 1962 when the winter tests were made, was 16 $\mu g/m^3$ while the average NO_2-concentration during May and June 1962 was only 6 $\mu g/m^3$. These investigations were also extended to the absorption of other trace-gases, namely SO_2. During these tests we reached values up to 1.5 mg/l SO_4 in rain-water which can be attributed to SO_2-absorption.

Generally it can be concluded that an appreciable amount of soluble gases is absorbed in rain-water. On the basis of the results which we gained up to now it can be assumed that 25 to 40 % of the total NO_3-concentration found in rain-water at ground-level at Frankfurt/Main can be attributed to the absorption and irreversibel incorporation of atmospheric NO_2. These experiments will be continued with larger air-volumes and will be modified to represent the atmospheric conditions more realistically. For this purpose a closed chamber holding 1 m^3 of air will be constructed into which rain-water is sprayed. The droplets are then recirculated for several times after fall-out.

Investigation on the concentration of trace-substances in precipitation-elements as function of drop-size

The investigations of the chemical concentration of precipitation showed that the concentration of different chemical compounds in precipitation samples collected within clouds is not related to the quantity of rain fallen. This was demonstrated in our Annual Report No 2, 1961 for Zugspitze and for the rain-samples analyzed in 2000 mtrs. on the Hawaiian mountains during project "shower". We concluded therefore that the processes effective below the cloud-base, namely wash-out and partial evaporation of droplets differentiate the salt-concentration of rain-drops with regard to the quantity of rain. The consequence of this is the assumption that within the cloud all drops have approximately the same concentration of trace-substances irrespective of their size, but below the cloud-base the concentration of trace-substances in rain-drops will show differences with respect to drop-size.

Little research on measurements of chemical trace-substances as function of the size of rain-drops has been carried out yet. The only investigation in this line has been performed by J.S. Turner (8) in Australia. Turner separated rain-drops into six or seven size-ranges using a modification of the raindrop spectrograph described by Bowen and Davidson (9). Turner investigated the sodium-concentration of the drop-samples. He found that in most cases smaller drops have a higher salinity than large drops. In agreement with our findings Turner states that the samples collected near the cloud-bases have a salinity relatively independant of drop-size. The majority of cases investigated by Turner originated from warm clouds with sea-salt as the major chemical component. It is therefore desirable to repeat these measurements in connection with our investigations more systematically and particularly under conditions where a variety of chemical traces as aerosols and gases are offered. For this purpose we are using a rain-drop spectrometer constructed by Stierstadt and Kadereit (10) which is shown in Fig. 6. The principle of this instrument is the following: The raindrops entering by a slit are deflected in a horizontal wind-stream. The deflection depends on the size of the drops, the smaller being more deflected than the larger ones. The rain-drops are collected in four glass-basins in the bottom of the horizontal channel. The deflection of the drops can be calculated:

$$D = \frac{3}{8}\, c\, \frac{\rho_A}{\rho_W}\, v^2 h\, \frac{1}{r^2 v_z}$$

$c \cong 0.5$ ρ_A = density of air
ρ_W = density of water
h = height of horizontal channel
r = radius of drops
v_z = fall-velocity of drops

Comparison of theoretical and experimental studies showed the following results with regard to the separation of drops of different size in the four sampling-basins

	Diameter of rain-drops in mm	
	theoretical	experimental
Basin I	$d > 0.72$	$d > 0.7$
" II	$0.92 > d > 0.56$	$1.3 > d > 0.5$
" III	$0.61 > d > 0.48$	$0.9 > d > 0.4$
" IV	$0.51 > d > 0.42$	$0.7 > d > 0.3$

We have installed this instrument during fall 1962 on our Taunus observatory "Kleiner Feldberg" since the samples gained in Frankfurt were too small for evaluation. The average amount of rain which falls on the Taunus ridge is about twice that falling in Frankfurt/M. We can therefore hope to collect larger samples suitable for analysis on Taunus observatory.

Continuous records of the concentration of trace-substances in rainwater

Continuous records of the electrolytical conductivity during individual rainfalls have been systematically continued during 1962. In addition to the electrolytical conductivity, which is an indicator for the total concentration of soluble inorganic trace-substances, we were able to extend our measurements to pH-value and natural short lived ß-radioactivity of rain. These three components are now simultaneously recorded. The rainwater runs through a small-steel-basin below a pan-cake counter (Model 1001T of Anton Electrics). These are flat counter tubes with a large diameter window suited for low intensity-measurements. After measurement of the ß-activity the rain-water is led into the cell for measurement of acidity and finally into the third cell for measurement of the electrolytical conductivity. The instrumental set-up for the measurement of natural short-lived ß-activity during the course of individual rainfalls is similar to that described by W. Jacobi (11) to whom we are grateful for advice in this matter. Each of the three cells has a volume of not more than 10 cm^3, so that all fluctuations of the chemical constitution of the rain occurring during the rainfall are recorded. Figs. 7 and 8 show a schematic diagram of the instrumental set-up.

Figs. 9 and 10 show two more cases of the fluctuations of the concentration of trace-substances in rainwater during the course of individual rainfalls. Fig. 9 shows the case of a rainfall connected with the passage of a warm-front. Typical for these situations is the decrease of the electrolytical conductivity after the onset of rain. After the decrease it remains more or less constant during the further course of the rain. We have also entered in Fig. 9 the record of the SO_2-concentration in the ground-layer of the atmosphere which shows a decrease during the rain. This drop of concentration can be attributed to wash-out. Fig. 10 shows the electrolytical conductivity during showery weather. The intensity of rain fluctuates very strongly and the same applies to the electrolytical conductivity of rain-water. It can be assumed that here each shower is generated from a fresh cell. During the growth of the precipitation-elements in each one of the shower cells the mechanism of incorporation of trace-material into the cloud-elements was active. This explains the increase of the electrolytical conductivity which is connected with each increase of rain-intensity. As we have seen in some cases reported in Annual Report No 2 this is not always the rule. In contrary we observe frequently a decrease of electrolytical conductivity connected with an increase of rain-intensity. We may assume that this combination occurs when the increased amount of rain/time is produced by the same precipitating cell.

In Figs. 11 and 12 we present two cases of our combined records of components related to the chemical constitution of precipitation which started during this autumn. Fig. 11 shows two cases of rainfall of showery character during September 1962. On 6 Sept. 1962 heavy fluctuations of the electrolytical conductivity were recorded. High values of the electrolytical conductivity are related to low values of rain-intensity. It is interesting to note that an increase of the electrolytical conductivity is connected with higher acidity of the rain-water expressed by low pH-values. During this rain pH-values of 3,3 are reached, which means "very acid" in the terminology given by F. Steinhauser (12). Steinhauser found for precipitation sampled in Vienna that 11 % of all cases were "very acid". All peaks of the electrolytical conductivity are related to fluctiations of pH-value. But as can be seen in Fig. 12 on 13 Nov. 1962 at 5.30 hrs an increase of the electrolytical conductivity can also be connected with a sudden increase of the pH-value, that means with a decrease of acidity. In the top part of Fig. 12 we have entered the total ß-radioactivity measured during the rainfall. The background-count is about 40 to 50 Imps./min. Each peak of the electrolytical conductivity of the rainwater is also related to an increase of the ß-activity. The decrease of the radioactivity however is much slower due to the decay of radioactive aerosols deposed in the sampling-basin.

While the radioactivity of the rainwater is mainly due to incorporation of radioactive aerosol-particles, the electrolytical conductivity can be caused by soluble components of aerosol as well as by gaseous traces. We believe that the combined analysis of these different components of rainwater will most certainly produce better information on the mechanism of rain-out and wash-out.

Concluding remarks

The investigations carried out since the publication of Annual Report No 2 in August 1961 have yielded new results on the distribution of trace-substances in cloud- and rainwater. They show that approximately 50 to 80 % of the concentration of trace-substances measured at ground-level have been incorporated within the clouds. The exact amount depends much on the quantity of rain fallen during each individual case of precipitation.

Further efforts have been made to determine the importance of trace-gases for precipitation-chemistry. Preliminary results show that in the case of the NO_3-concentration in rain nearly 40 % may be attributed to absorption of gaseous NO_2 under favourable conditions. These investigations will be continued with an instrumental set-up representing closer atmospheric conditions.

More research is needed to gain quantitative results for the distinction of the effect of wash-out below the cloud-base and of partial evaporation of droplets during their fall through the cloud-free zone. One approach is the analysis of drops as a function of drop-size by means of a rain-drop spectrometer. It will also be necessary to conduct more experimental and theoretical research on the partial evaporation of drops. This will be done during the coming year.

Continuous records of three independant components during the course of rainfalls are now being carried out by which we are able to gain a very comprehensive picture of the chemical constitution.

A further investigation of the results of these records will be conducted on possible relations between the fluctuation of the different elements and the altitude of cloud-ceiling which determines the zone of free fall of precipitation-elements.

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List of Figures

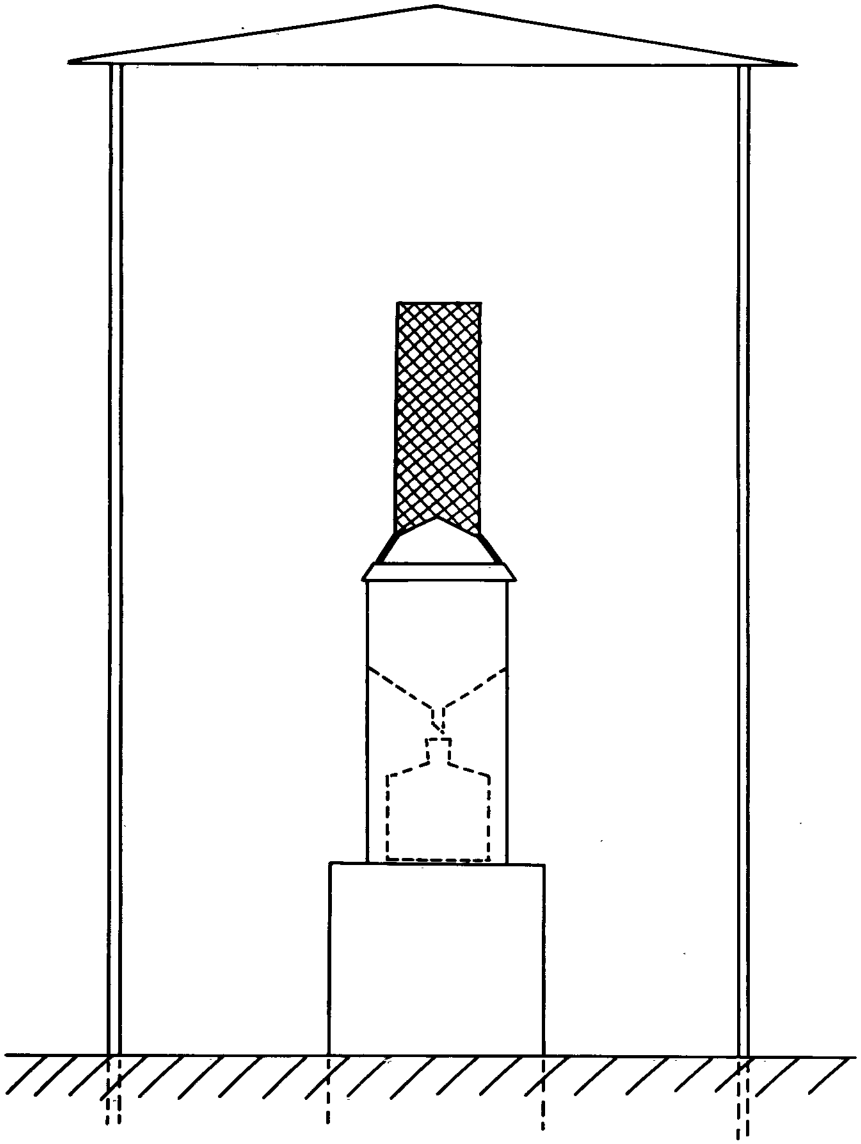


Fig.1

Absorption von atmosphärischem NO_2

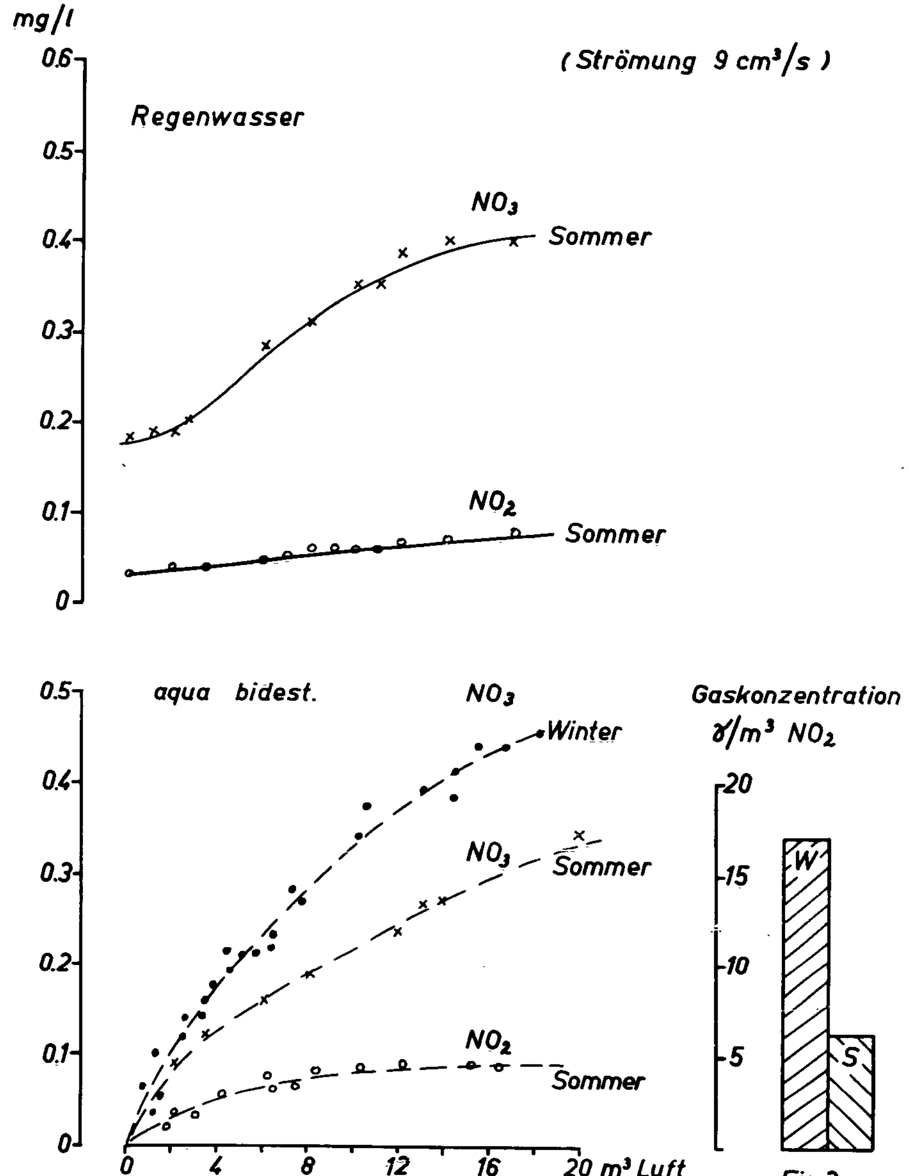


Fig.2

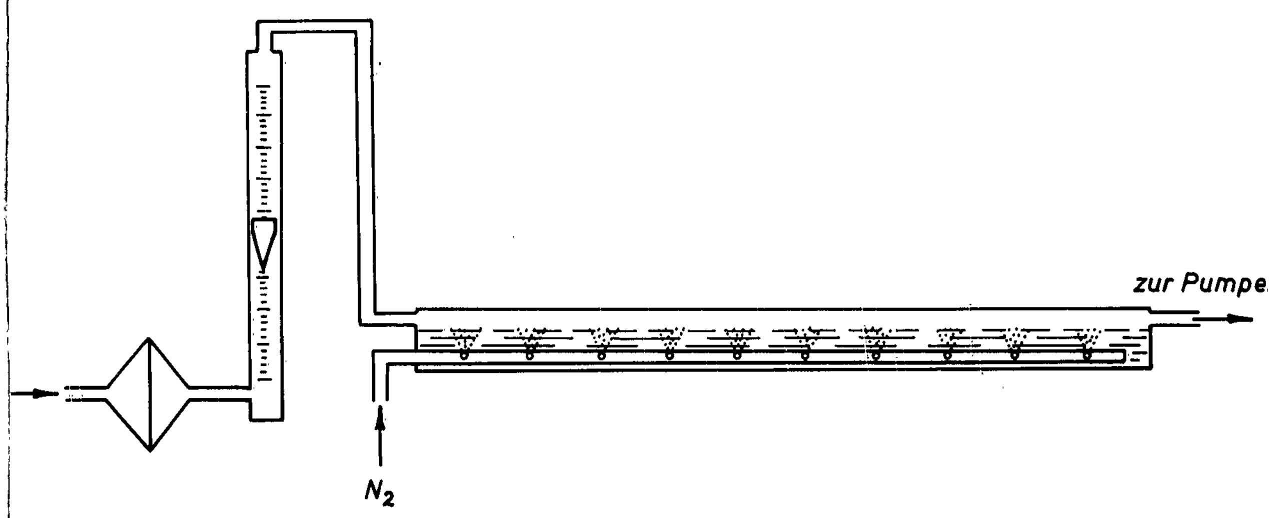

zur Pumpe
N_2

Fig.3

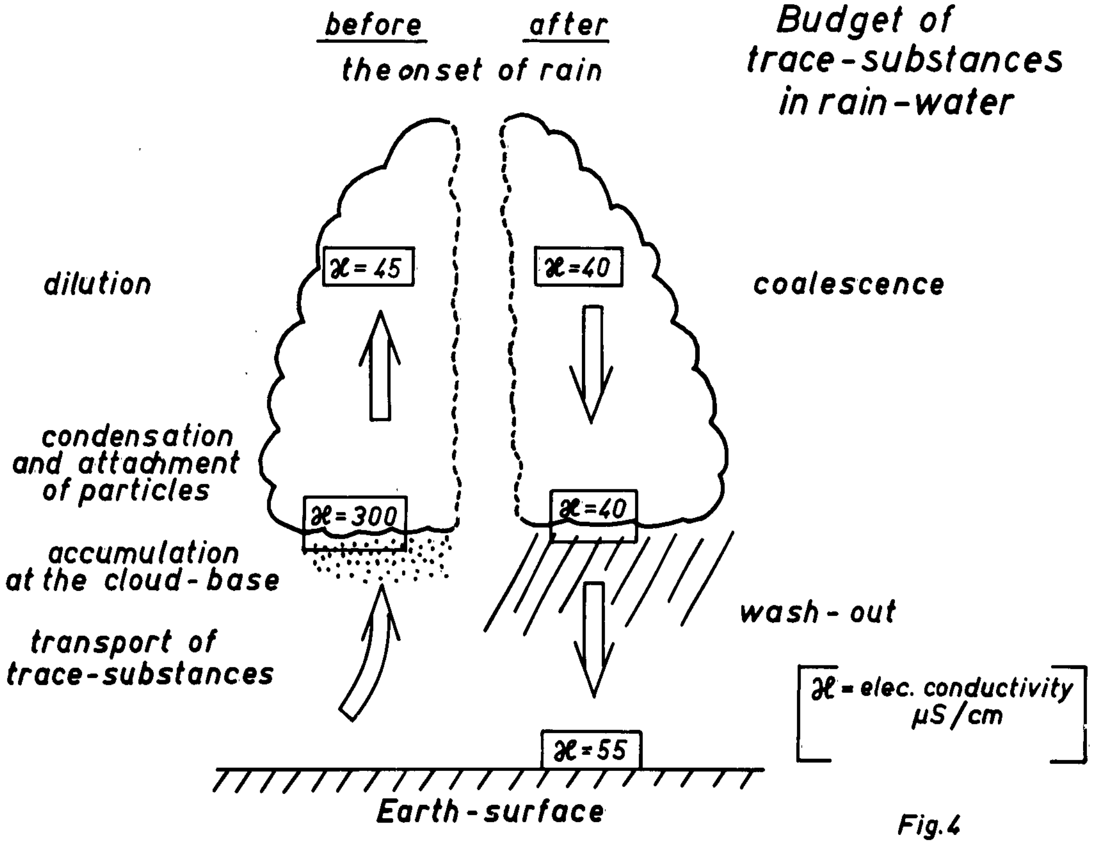
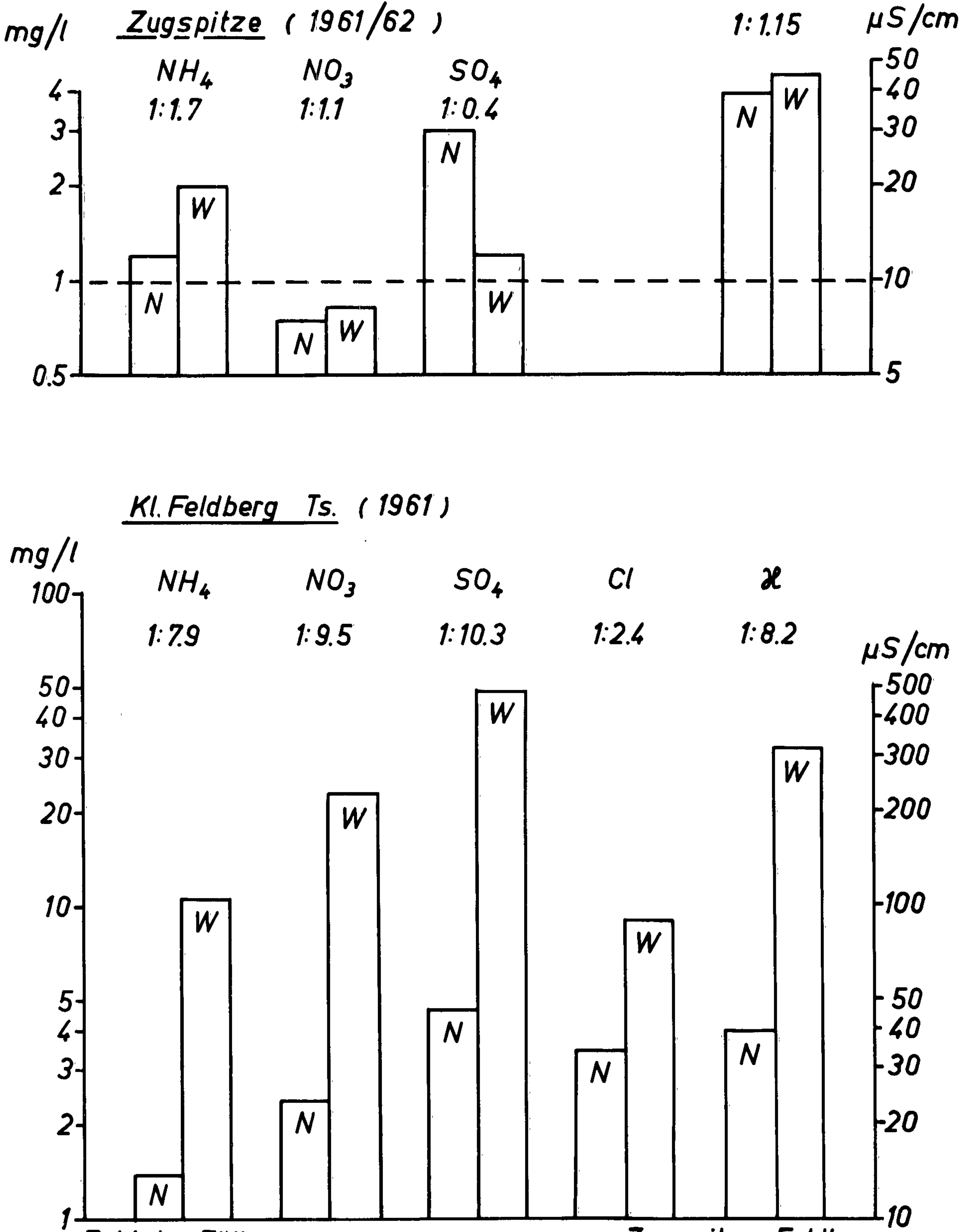

before
after
the onset of rain
Budget of trace-substances in rain-water
dilution
$\varkappa = 45$
$\varkappa = 40$
coalescence
condensation and attachment of particles
$\varkappa = 300$
$\varkappa = 40$
accumulation at the cloud-base
wash-out
transport of trace-substances
$\varkappa$ = elec. conductivity µS/cm
$\varkappa = 55$
Earth-surface

Fig.4

Spurenstoffkonzentration im Niederschlag (N) und Wolkenwasser (W)


Zugspitze (1961/62)

Kl. Feldberg Ts. (1961)

Zahl der Fälle	Zugspitze	Feldberg
Niederschlag (N)	94	70
Wolkenwasser (W)	27	40

Fig.5

Windkanal (Regentropfenspektrometer)

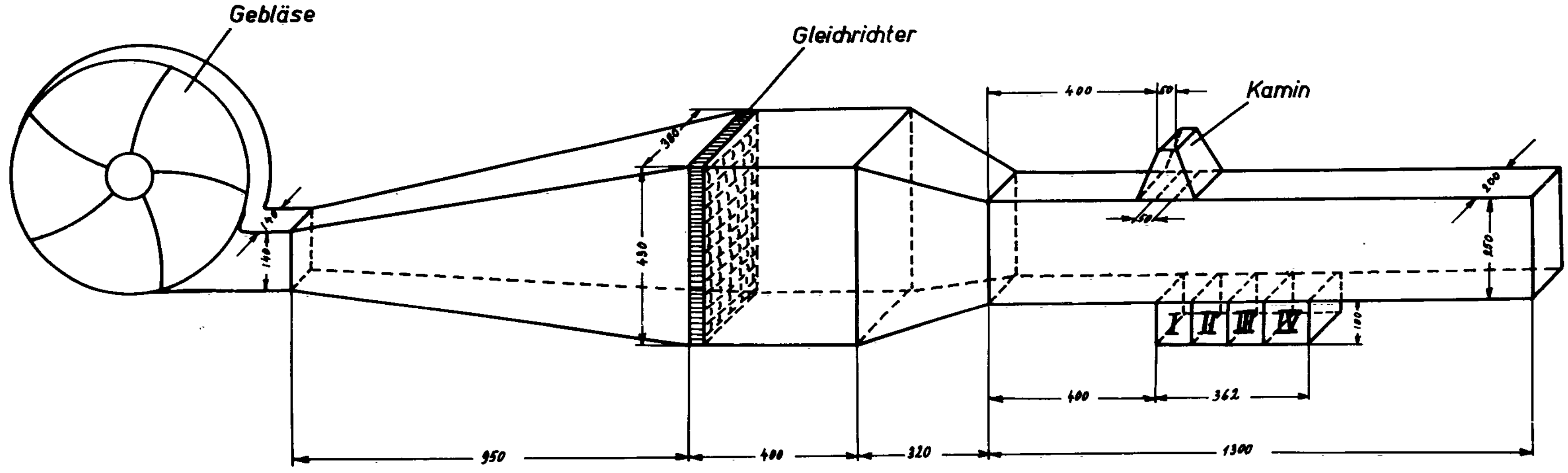


Fig.6

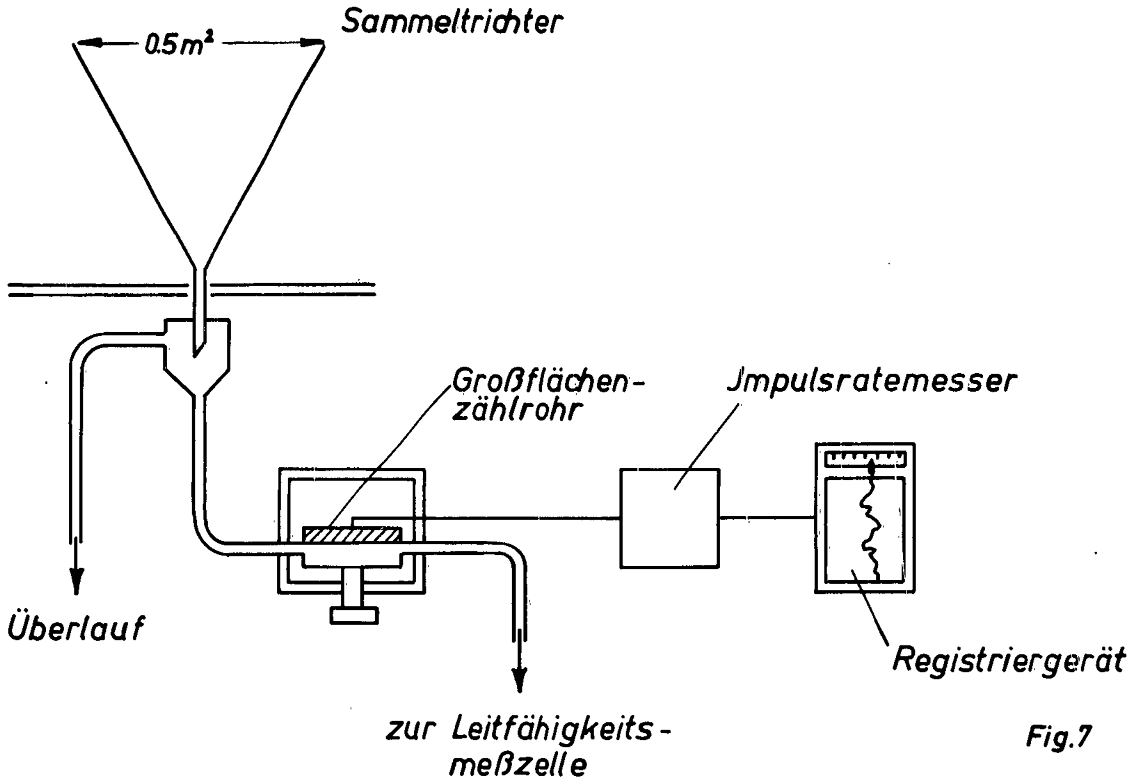
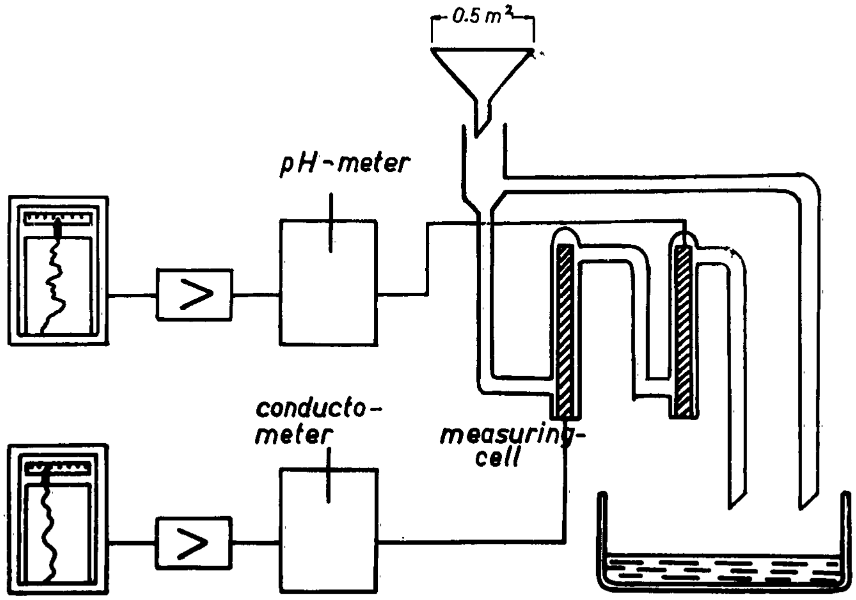


Fig.7



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

Fig.8

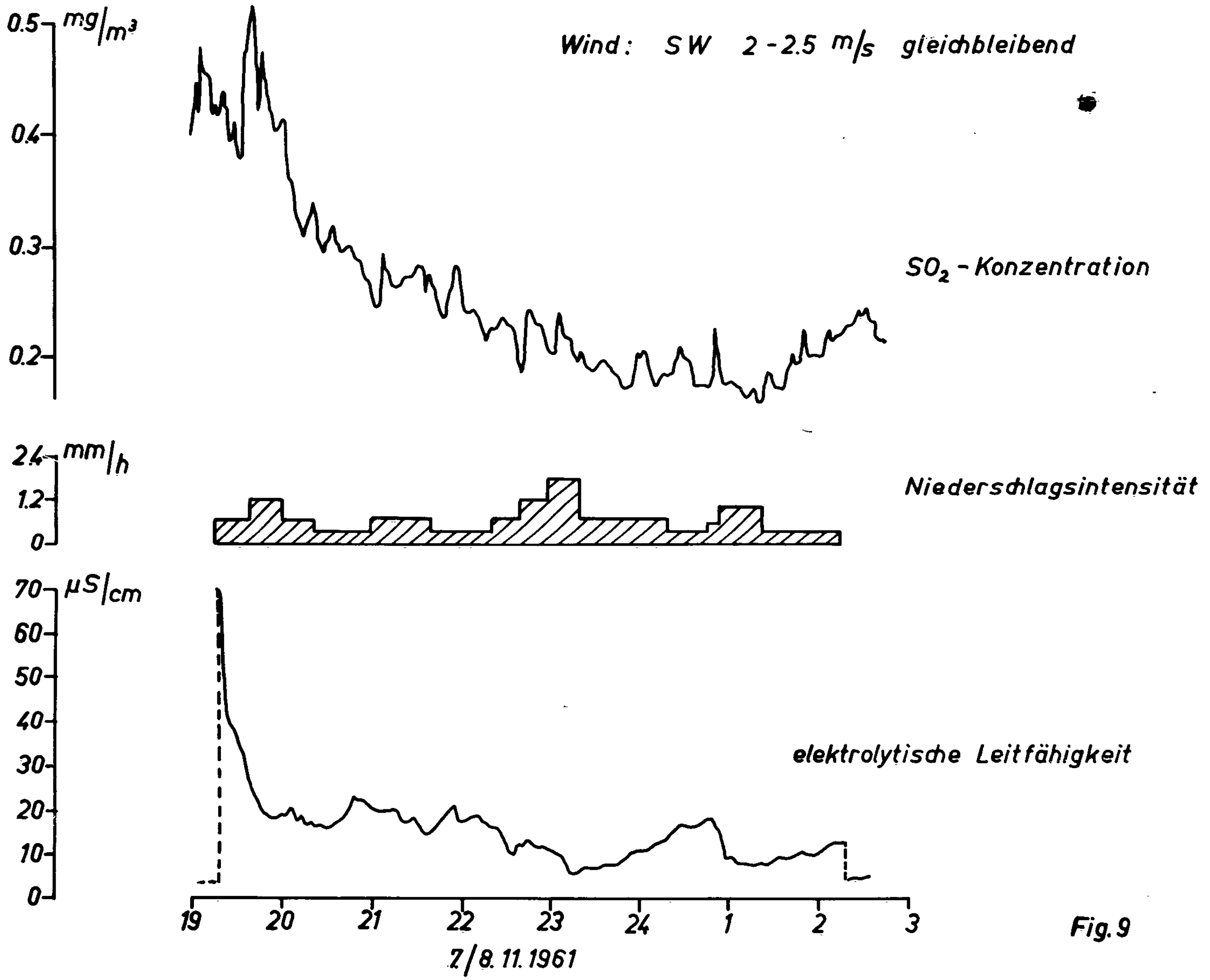

Wind: SW 2 - 2.5 m/s gleichbleibend
0.5
mg/m³
0.4
0.3
0.2
SO₂ - Konzentration
2.4
mm/h
1.2
0
Niederschlagsintensität
70
µS/cm
60
50
40
30
20
10
0
elektrolytische Leitfähigkeit
19
20
21
22
23
24
1
2
3
7/8. 11. 1961

Fig. 9

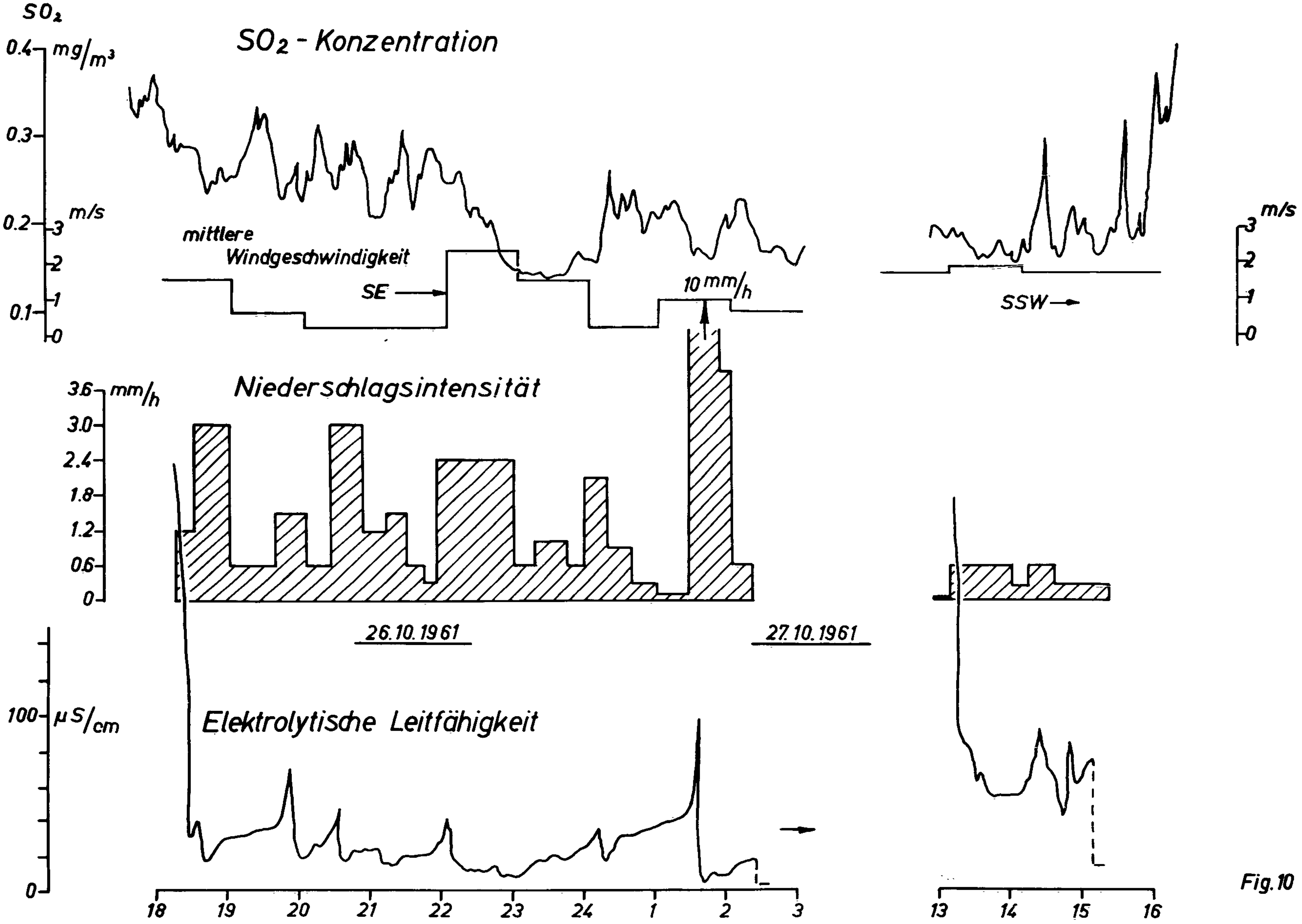

SO₂
0.4
0.3
0.2
0.1
mg/m³
SO₂ - Konzentration
m/s
3
2
1
0
mittlere Windgeschwindigkeit
SE →
10 mm/h
SSW →
m/s
3
2
1
0
Niederschlagsintensität
3.6
3.0
2.4
1.8
1.2
0.6
0
mm/h
26.10.1961
27.10.1961
100
0
μS/cm
Elektrolytische Leitfähigkeit
18
19
20
21
22
23
24
1
2
3
13
14
15
16

Fig.10

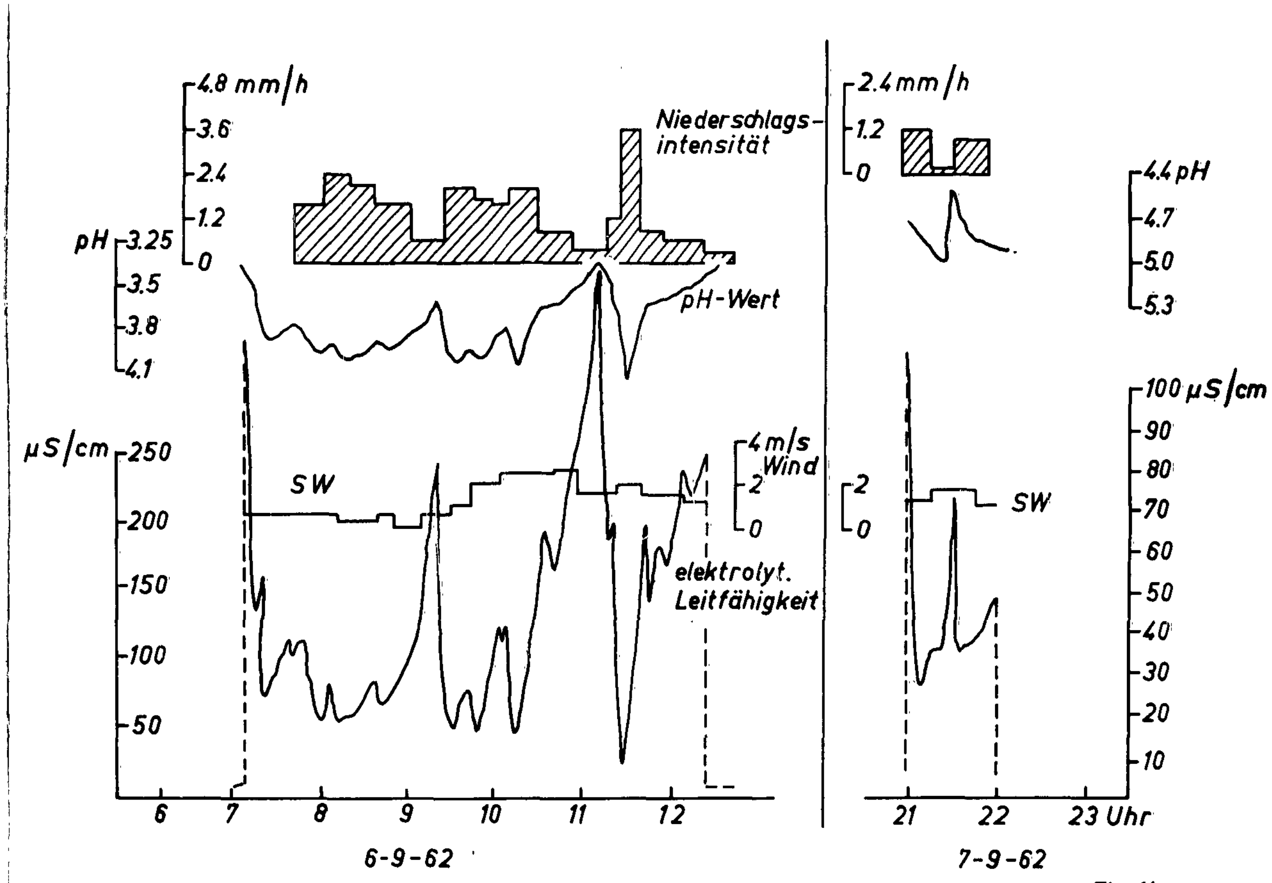

4.8 mm/h
3.6
2.4
1.2
0
Niederschlags-intensität
pH
3.25
3.5
3.8
4.1
pH-Wert
µS/cm
250
200
150
100
50
SW
4 m/s
Wind
2
0
elektrolyt. Leitfähigkeit
6
7
8
9
10
11
12
6-9-62
2.4 mm/h
1.2
0
4.4 pH
4.7
5.0
5.3
100 µS/cm
90
80
70
60
50
40
30
20
10
2
0
SW
21
22
23 Uhr
7-9-62

Fig. 11

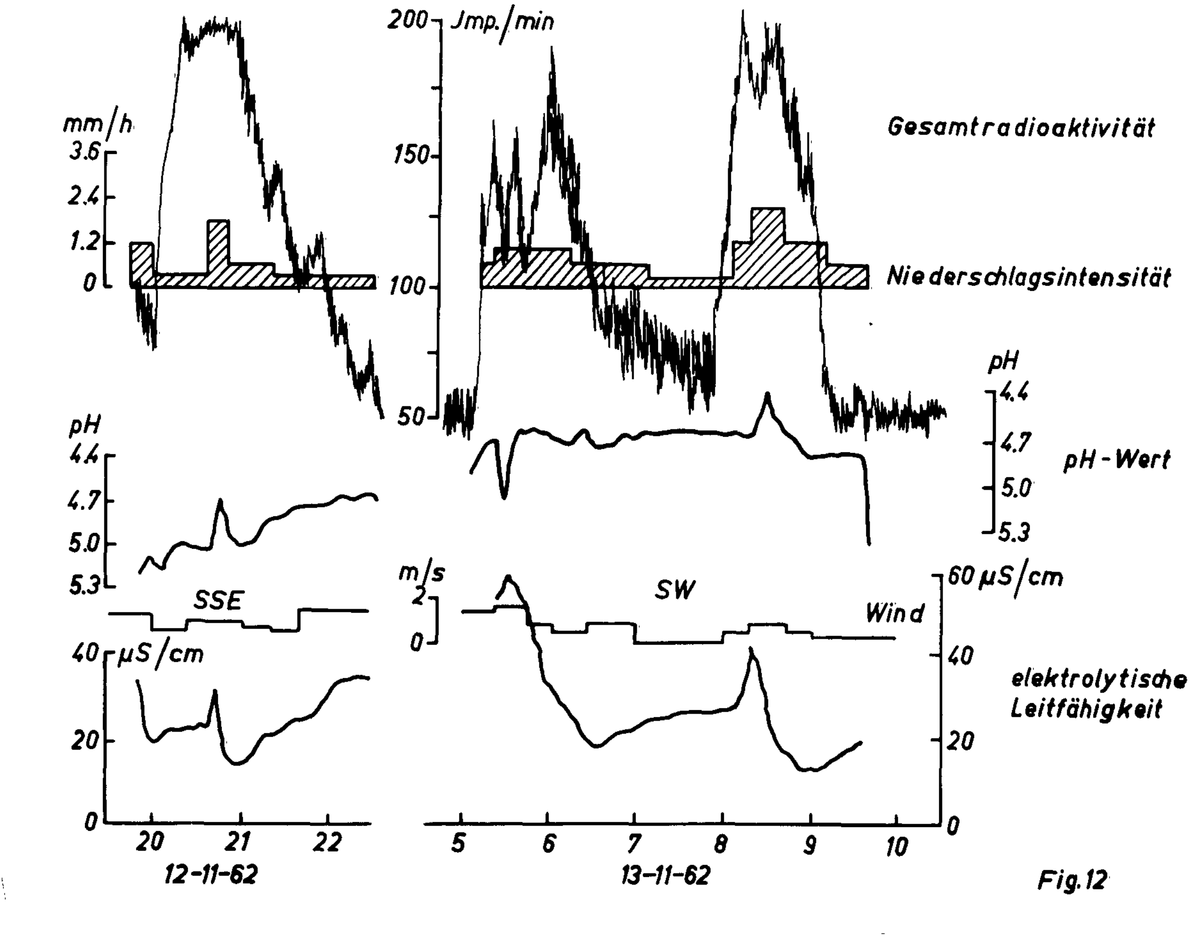

mm/h
3.6
2.4
1.2
0
200
150
100
50
Jmp./min
Gesamtradioaktivität
Niederschlagsintensität
pH
4.4
4.7
5.0
5.3
pH-Wert
SSE
m/s
2
0
SW
Wind
60 µS/cm
40
20
0
µS/cm
elektrolytische Leitfähigkeit
20
21
22
12-11-62
5
6
7
8
9
10
13-11-62

Fig. 12