Measurements of pH, and chemical analyses of rain-, snow-, and fog-water

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ABSTRACT

Since 1957 more than 200 samples of rain water have been analysed at the Meteorological Observatory of Dresden-Wahnsdorf (51,1° N, 13,7° E). At four mountain summit stations and one coastal station fog water was sampled and analysed.

The yearly mean of the pH has remained constant since 1958, while in western Europe Jessel found a decrease in the pH. There are no differences of the pH between summer and winter and between shower and rain.

There are no differences in the concentration of chemical traces between shower and rain, the seasonal difference is unimportant.

The concentration of traces including the artifical β radioactivity in fog water is larger about one order of magnitude. It is possible to estimate approximately the trace content of one cubicmeter of air from the trace concentration of the fog water and the water content of the fog, if the fog persists for a long time.

1. Sampling and analysis methods

At Wahnsdorf Observatory chemical analyses of individual rain occurrences have been made since July 1957, with additional determinations of pH. Precipitation is collected in a 0.82 m diameter polyethylene funnel the corresponding aperture being 0.528 m². The rim of the funnel is 80 cm above the grass of the Observatory measuring field.

With the beginning of a precipitation to be sampled the funnel is washed with distilled demineralized water, in order to prevent most of any polluting of the sample by dust and absorbed trace gases of the near-ground layer of air—though this will never be achieved entirely. If the air contains SO_2, this gas solves at the wet funnel walls during the rain, is oxidized by oxygen into H_2SO_4 thus increasing the sulfate content of the rain sample. After the rain has ceased the water is filled into a bottle which is then to be closed. The analysis of the samples covers the following data:

pH is measured by glass electrodes using known standard buffers.

Determination of chloride after Mohr. The sample is evaporated to about 1/10 of its volume on water bath.

Gravimetrical determination of sulfate, after evaporation. Colorimetrical determination of nitrate as 4 nitro-2-hydroxy benzoic sodium in a basic solution.

Colorimetrical determination of ammonia with Nessler reagent, if required after distillation by adding NaOH.

2. Results of rain analyses

(a) *pH*

The frequency distribution of 206 pH measurements is to be seen in Fig. 1. The mean value is 4.5. This is not only far below the neutral point, i.e. in the acid region, but also below the balanced pH of distilled demineralized water and the normal atmospheric CO_2 content which is 5.5 at 20°C (Barret & Brodin, 1955). In Vienna from March 1956 to December 1957 Steinhauser (1959) found the pH values 5–6 to be the most frequent range. Results found by Berg (1959) from Cologne and sur-

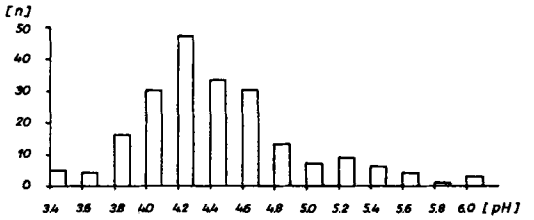

Fig. 1. Frequency distribution of 206 pH-values.

rounding area from autumn 1957 to summer 1958, scatter around the neutral point ranging from 3.4 to 9.9. In the Scandinavian network the pH values are around the above mentioned balanced pH of 5.5 (BARRET & BRODIN, 1955; EGNER & ERIKSSON 1955).

Major immission of sulfuric acid (H_2SO_4) from heating exhausts suggests an annual variation with a winter minimum which we were, however, unable to confirm. The winter average (October to March) is 4.41; the summer average (i.e. April to September) is 4.49.

CAUER (1956) found the pH in clean air to be lower than in urban air assuming the reason for this to be the absence of basic flaky ashes at remote measuring sites. The lower pH is assumend to be caused by the presence of HNO_3. Nitrations are found all over the year, as will be shown below.

Comparing the pH value from shower and rain precipitation, means of 4.6 and 4.4 are found. The lower value with continuous rain is possibly due to the longer sampling time and consequently the longer time of SO_2 loss of the air to the sample. However, this cannot be statistically confirmed.

Comparing the average pH value of the period 1958 to 1960 with the average of the period 1961 and 1962 in both cases 4.5 is obtained, with the 1964 annual mean value being 4.6.

This pH constancy contrasts to the results of a study by JESSEL (1964), who shows that in Federal Germany, with the exception of the North Sea coast, there was a substantial decrease of precipitational pH. The difference of both these results is suggested to be originated by the different type of pollution in the two areas. In Federal Germany and equally in the whole of Western Europe altogether solid fuel heating is being replaced by oil heating. In the GDR there is no such a switch-over. SO_2 emission with oil and coal heating is very similar in magnitude; however, with coal heating basic fine dust is emitted, which partly neutralizes the acid. In oil heating exhausts the sulfuric acid produced by SO_2 oxidation remains unchanged.

(b) Ion content

Mean values of rain analyses are compiled in Table 1. A comparison of showers and continuous rain does reveal only slight differences which, however, cannot be statistically proved.

TABLE 1. *Samples of precipitation in Wahnsdorf.*

Content in mg/l; M = mean value, n = number of single analyses.

	Cl	SO_4	NH_3	NO_3	pH
Shower					
M	1.6	10.8	2.1	2.0	4.6
n	99	97	117	117	71
Rain					
M	1.5	12.5	1.9	2.3	4.4
n	188	185	207	204	135
Winter (X – III, all samples)					
M	1.7	13.2	2.0	2.4	4.4
n	137	142	161	156	104
Summer (IV – IX, all samples)					
M	1.4	10.6	1.9	2.9	4.5
n	147	140	164	165	105

The chloride and ammonia content is only slightly larger in showers, while there is a somewhat larger portion of the remaining minor components in continuous rain. The already mentioned continuous rain pH value corresponds to the higher amount of sulfate, which presumably originates from the absorbed and oxidized SO_2. A comparison of winter (October to March) and summer (April to September) precipitation shows, as has been expected, a higher portion of minor components in winter —the difference, however, being very slight and not to be proved statistically. The higher nitrate content in winter is evidence for the nitrate formation by atmospheric-electric processes to be without significance.

II. Fog water analyses

1. SAMPLING AND ANALYSIS PROCEDURES

For an analysis of near-ground air pollution the investigation of falling precipitation does quite obviously not furnish sufficient details. It will be necessary to analyse condensed water which was produced in the basic layer. To this end, fog water collected at mountain and coastal stations has been investigated. The results are substantially different to rain water analyses.

Sampling the material which in any case must be unpolluted by the station's heating

TABLE 2. *Mean content of traces in fogwater.*

Content in mg/l; M = mean value, n = number of single analyses.

	Cl	SO_4	NH_3	NO_3	K	Na	Ca	pH
Grosser Inselsberg, Thüringer Wald, 916 m								
M	8.3	63.0	10.8	9.0	—	—	—	—
n	30	30	29	9	—	—	—	—
Brocken, Harz, 1152 m								
M	7.3	37.2	12.1	13.9	3.4	6.8	4.4	5.1
n	18	18	19	19	19	19	19	19
Collmberg, 315 m, sampled at the television-tower 370 m								
M	20.7	158.5	35.7	11.8	—	—	63.6	4.2
n	12	12	11	11	—	—	8	9
Kap Arkona, 46 m, Baltic Sea								
M	61.7	89.3	39.7	28.1	9.5	34.5	15.0	3.8
n	42	40	42	42	27	28	28	42

exhausts and which, further, must not include fallen precipitation from rain or snow is done in a very simple way when there is frost, i.e., by breaking off soft rime or rime and melting it. In frost-free periods fog samplers, i.e. wooden frames covered with pervious cloth, are used. The precipitated water then drops from the corner of the frame into a sampling bottle beneath. The effective size of the exposed surface is 1 m². In such a way on the Inselsberg summit tower 8 litres had been caught within 2 hours, with strong winds prevailing, and rain being absent.

Five stations sent fog water samples to the Observatory Wahnsdorf. Kap Arkona (54,7° N 13,4° E) is a 46 m high ledge of the bluff at the northern point of the Rügen island. Mount Brocken (51,8° N 10,6° E) is the highest top of the Harz mountains, inspite of its low height of 1155 m surpassing the climatic forest line. The Inselsberg (50,9° N 10,5° E), 916 m high, at the NW of the Thuringian Forest is covered by mixed forest (beeches, firs). The 824 m Geisingberg (50,8° N 13,8° E) and the flat-topped 890 m Lugstein (at a distance of 5 km) in the eastern Erzgebirge are also wooded. The Collmberg (51,3° N 13,0° E) is a wooded hill in the flat country between Dresden and Leipzig, its altitude being only 316 m. Sampling is done on towers, which provides for the heating exhaust gases being excluded entirely from the sampling spot. The methods of analysis are the same as are applied to precipitation sampling. Determinations of alcali by flame photometry are added, calcium is examined partly in the same way partly by gravimetric methods.

2. RESULTS

Means of water analyses of each station are listed in Table 2. The higher percentage of minor components is conspicuous. The difference comes very near to the tenth power. The external appearance of each of the fog water samples is marked by a dark, in many cases even black colour. The pH is lower than that gained from rain water samples, with the exception of Mount Brocken. However, whether these high values are acceptable or some of the samples had been polluted during the melting process is doubtful. The pH of the 42 Kap Arkona samples is very low—in 6 cases lower than 3.0 with a mean value of all samples of 3.8. For the Inselsberg analyses there was no pH measuring device available. The highest percentage of minor traces is found in the Collmberg fog water samples. These values are typical for the basic layer of the whole industrial area of the northern Saxony lowlands. In the vicinity of the measuring point there is, 10 km to the west, a closed forest area, in the remaining directions there are cultivated fields up to the horizon. Power plants, briquetting plants, and major chemical plants are more than 50 km away.

The fog water samples collected on the tops of the Thuringian Forest, Erzgebirge and Harz contain a smaller amount of minor traces than those collected in the lowlands and at the coast, which is, however, by multiples in excess of the content of rain water samples. The concentration of the minor traces is variable, which is due to the varying air masses, exchange and fog water content. There is, in the Inselsberg series, a conspicuous dependance of the content of minor traces on meteorological conditions which prevailed at the time of sampling. The sulfate content, which is mainly man-made, is with east wind prevailing higher than with westerly winds, although to the west there is one of the largest industrial areas of Europe—the Ruhr District. However, the westerly winds are of higher speed and marked by a more pronounced turbulence as compared with easterly winds. Thus, the enrichment of

the basic layer with sulfur in the Ruhr District, which is 200 km away, is of less importance than is the Central German industrial area at nearly equal distance. The highest content of sulfate 179 mg/l had been observed in soft rime deposited between March 11 and 13, 1955. There was high pressure over Scandinavia producing, for several days running, light winds from the NE quadrant with a stable stratification. The lowest value 11 mg/l of sulfate was observed on November 8, 1954. The mountain was in unstable, highly turbulent air at the rear of a cyclone, centered near the mouth of the Oder river, which was part of series of cyclones moving from Ireland to Finland.

Quite unexpectedly, the content of minor traces is nearly equal in the Inselsberg summer und winter series. At the remaining stations there are hardly any values available other than of the cold season. During the heating season a much higher content of sulfate should be expected. However, we are not supposed to conclude from the equal content of sulfate occurring in summer and winter that on the average of all days in summer the pollution of the air is equal in the winter season. Summer days with low-lying clouds are a rare event and associated with rather low exchange. The selection—so we may conclude—is of a particular nature in summer, which is not the case in winter, i.e. the period marked by low clouds. Further, there is the unavoidable error occurring during the sampling: due to the difference of vapour pressure between supercooled water and ice, hoar frost contains apart from the precipitated fog droplets sublimation water, which presumably contains a smaller content of minor traces. We might expect that with equal content of minor traces in the air hoar frost does contain a smaller percentage than fog.

III. Air pollution estimation from fog water analyses

From the analysis data and the greyish-black colour of the fog water samples one is inclined to suggest that fog formation always occurred in a highly polluted urban or industrial atmosphere, not, however, in a sparsely populated coastal region or over the wooded mountains. From a rough calculation it can rather be seen that in an atmosphere with normal content of minor traces persistent fog must adopt the concentration of minor traces observed.

When fog or stratus layers, lifted from the ground, persist for hours or even days, the aerosol particles partly are condensation nuclei, partly touch the droplets due to the Brownian motion and the Stefan flow. Gases solve proportionally according to Dalton's Law. They can, however, when assimilated in the droplets, be absorbed entirely by them, as for example SO_2 which in aqueous solution rapidly oxidizes, then being out of balance with the gaseous phase.

Assuming, as a first approach, that the whole content of minor traces has changed into the aqueous phase and that the liquid water content in fog is 0.5 g/m³—as was determined from the psychrometer measurements made on the mountains—fog analysis permits the minor traces content of air to be determined. If, for instance, in the mountains the content of sulfate in water is 50 mg/l there will be 25 μg/m³ in the air. This value is rather small, considering the Wahnsdorf annual mean being about 200 μg/m³. With a smaller water content of the fog the enrichment is larger accordingly. If the water content is 0.1 g/m³, as might be the case rather frequently in sea fog, and the content of sulfate 150 mg/l in water, the air has a content of only 15 μg/m³.

If in the same way the content of minor traces of the air is estimated in which falling precipitation forms, we gain rather small values, even if it is taken into account that in rainy clouds the water content can be 2 to 4 times larger. One is inclined to suggest that the air at the precipitation-forming level is cleaner than near the ground, provided the results of radioactivity measurements do not necessitate this conception to be altered. MARQUARDT (private communication) in 1958 compared artificial atmospheric radioactivity in Wahnsdorf with the fog water activity of the Geisingberg (40 km away). The result is that in the same way as could be shown above as to inactive minor traces, the activity of the air can be determined at reasonable approximation from the activity of fog water, which means that the activity is largely absorbed by the aqueous phase. In 1964 he found on Mount Brocken the activity of fog to be one order of magnitude in excess of the one of rain water (Table 3). This is rather surprising, as after the 1963

TABLE 3. *Artificial radioactivity in fog and rain sampled at the Brocken* (W. Marquardt, 1964).

Fog water		Rain water	
Date	nc/l	Date	nc/l
3.VI. 1964	3.5	2.VI. 1964	0.33
7.VI.	7.4	5.VI.	0.36
9.VI.	4.0	7.VI.	0.39
15.VI.	17.6	29.VI.	0.21
16.VI.	4.5	Mean value	0.32
19.VI.	3.4		
20.VI.	3.9		
22.VI.	8.8		
23.VI.	7.1		
24.VI.	3.9		
28.VI.	7.7		
29.VI.	5.5		
Mean value	6.4		

atomic test ban the source of artificial radioactivity was in the stratosphere with the gradient in the atmosphere suggested to be directed downwards. The smaller radioactivity in precipitation falling from upperair layers shows that when precipitation forms, there is a smaller amount of minor traces changing into the aqueous phase than with formation of stable, non-precipitating fog or stratus layers. The length of time the precipitation elements stay in contact with the air is rather short as compared to floating droplets in a stable fog.

As in fog water the minor traces of the air are enriched by more than 6 orders of magnitude, fog water analyses can be utilized for the determination even of such minor traces which for direct measurements require a rather high amount of work. Hence, it seems to be worth while to develop a routine technique of sampling and cloud-water determination in stable cloud layers, as cloud-water analyses do furnish more qualified information on the content of minor traces of the air than can be gained from investigations of falling precipitation.

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ИЗМЕРЕНИЯ pH И ХИМИЧЕСКИЙ АНАЛИЗ ВОДЫ В ДОЖДЕ, СНЕГЕ И ТУМАНЕ

С 1957 г. в Метеорологической обсерватории в Дрездли-Вансдорфе (51,1°С, 13,7°В) было исследовано более 200 проб дождевой воды. Пробы брались и анализировались на 4 станциях, расположенных на горных вершинах, и одной станции на побережье, для исследования воды в тумане.

Среднегодовое значение pH оставалось постоянным, в то время как в Западной Европе Jessel нашел, что имеет место уменьшение pH. Значение pH одинаково зимой и летом, в дожде и ливне. Концентрация химических примесей также одинакова в дожде и ливне, а сезонное различие не существенно. Концентрация примесей обладающая искусственной B-радиоактивностью на один порядок больше в воде из тумана, чем из дождя (ливня).

Если туман существует долго, то можно определить содержание примесей в 1 м³ воздуха, определяя концентрацию примесей в воде и концентрацию воды в воздухе.