On the chemical composition of cloud water

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(Manuscript received October 12, 1965)

ABSTRACT

In the article the chemical composition of the cloud water collected in the different regions of the USSR is considered. On the basis of their analysis and generalization the main characteristics of chemical content have been obtained. The total ion amount of cloud water slightly differs from that of precipitation, its chemical composition being different. A great influence of industrial pollution on the chemical composition of cloud water is to be noticed.

For the last 10–15 years the investigations of chemistry of atmospheric precipitation have been widely developed. The interest attached to this problem has been stimulated by the requirements of hydro- and agrochemistry, hydrogeology, geochemistry, as well as meteorology in connection with the study of physics and chemistry of clouds and precipitation.

At present rather extensive data have been obtained and careful atmospheric chemistry investigations have been carried out in such countries as Sweden, the U.S.A., Czechoslovakia, and the German Democratic Republic. These investigations are generalized in the works by ERIKSSON (1959, 1960), JUNGE (1963), MACKÝ, PODZIMEK & ŠRÁMEK (1959), MROSE (1961).

In the USSR considerable attention has been paid to this problem in the time of the International Geophysical Year. In the wide territory of the Soviet Union a collection of atmospheric precipitation samples has been organized and on the basis of their analysis and generalization spacious characteristics of precipitation composition have been obtained. Later on the work has been continued and extended considerably. The results of investigations on the question have been published in the articles by V. M. DROZDOVA, O. P. PETRENCHUK & E. S. SELEZNEVA (1961), V. M. DROZDOVA (1962), O. P. PETRENCHUK & E. S. SELEZNEVA (1962) and the monograph by V. M. DROZDOVA, O. P. PETRENCHUK, E. S. SELEZNEVA & P. F. SVISTOV (1964).

The atmospheric precipitation receives its constituents from the moment of water vapor condensation on the condensation nuclei and of the formation of cloud particles. Therefore, the knowledge of composition of water taken directly in the clouds is naturally of great importance. However, such data are rather insufficient up to the present time. This has been accounted for by method difficulties arising from taking cloud water samples. At the Main Geophysical Observatory the investigations of the chemical composition of cloud water are carried out under study of air chemistry.

The first data about the composition of the cloud water in the free atmosphere have been obtained by GRABOVSKY (1951) and SHMETER (1952). They considered mainly the chloride content in the supercooled clouds. However, since the atmospheric precipitation contains the different constituents it is important to estimate their concentration as well as in the cloud water.

For collection of cloud water samples under temperature above and below zero special devices have been designed (V. M. DROZDOVA, O. P. PETRENCHUK, E. S. SELEZNEVA & P. F. SVISTOV, 1964; O. P. PETRENCHUK & N. N. ALEXANDROV, 1966). They permitted to receive water quantity required for satisfactory analysis during a comparatively short time. Using this technique about 150 cloud water samples related to different regions of the European Territory of the USSR (ETU) have been obtained. The cloud water samples have been taken in the environs of the cities Leningrad, Archangelsk, Narjan-Mar, Kiev, Dneprope-

TABLE 1. *The mean composition of precipitation samples (Pr.) and of cloud water samples (CW) in different regions.*

Location	Sample	Concentration mg/l								pH	$\lambda \cdot 10^6$ Ω^{-1} cm^{-1}	Total	Cl′/Na·	SO_4''/Cl′	No. of samples
		SO_4''	Cl′	NO_3'	$NH_4^·$	Na·	K·	$Mg^{··}$	$Ca^{··}$						
North of ETU	Pr.	3.6	3.4	0.6	0.5	2.2	0.6	0.2	0.7	5.5	29	11.8	1.5	1.06	
	CW	0.6	6.3	0.1	0.6	2.4	1.7	1.0	0.4	5.3	30	13.1	2.6	0.09	16
North-west of ETU	Pr.	6.2	1.1	0.5	0.7	1.3	0.8	0.2	1.1	5.2	28	11.9	0.8	5.64	
	CW	6.0	2.5	0.5	0.9	1.2	0.8	0.2	0.6	4.7	28	12.7	2.1	2.40	29
South-west of ETU	Pr.	14.3	1.4	0.8	0.7	1.6	0.6	0.4	6.0	6.1	62	25.8	0.9	10.20	
	CW	8.9	2.1	0.8	1.8	0.7	0.6	0.5	1.0	4.8	40	16.4	3.0	4.24	46
Sea water[a]													1.8	0.14	

[a] The salinity of various seas is somewhat different but the ratio of the main ions remains constant.

trovsk and also during the horizontal flights carried out 1961–1964 on the following routes: Leningrad–Archangelsk–Narjan–Mar–Pechora; Leningrad–Minsk–Kiev–Dnepropetrovsk–Odessa.

On the whole one can distinguish three large sampling sites: north of ETU (environs of Archangelsk and Narjan–Mar), north-west of ETU (environs of Leningrad) and south-west of ETU (environs of Kiev and Dnepropetrovsk). About 100 samples have been collected in these regions.

The mean content of cloud water samples and the mean data of chemical composition of precipitation in these regions are given in Table 1, the former being compared to the latter ones. It should be noted that Table 1 does not include the heavily contaminated samples that will be considered in detail below.

One can see from the Table that in general total ion amount of cloud water samples in all sites except south-west differs slightly from that of precipitation, their chemical composition being different.

In the cloud water of north regions a very small concentration of sulfate and nitrate is observed and chloride and sodium are predominating ions. Such relation of constituents reflects apparently the vicinity of the sea coast and the absence of important industrial pollution. In the west and south-west of the ETU affected by the industrial pollution the concentration of SO_4'' in cloud water considerably increases; however, it is lower than that of the precipitation. The concentration of Cl′ is also high here.

The ratio SO_4''/Cl′ for all the examined regions essentially exceeds its value of 0.14 in sea water. As the presence of SO_4'' has been caused on the whole by industrial pollution one can see its great influence not only on the composition of precipitation but on that of cloud water.

The ratio Cl′/Na· differs both in the precipitation and in cloud water from its value of 1.8 in sea water and is to be paid much attention to. It is as a rule smaller than 1.8 in precipitation and larger in cloud water. It is interesting to note that some authors (E. ERIKSSON, 1959, 1960; JUNGE, 1963) have the ratio in precipitation less than 1.8 even in the immediate vicinity from the sea coast.

Some of the available mechanisms have been suggested for the explanation of this fact (H. CAUER, 1949; E. ERIKSSON, 1959, 1960). They involved a possible escape of Cl′ or Na· addition from continental sources. Since the presence of additional Na· sources in the vicinity of the sea coast is unlikely it is supposed that the escape of gaseous chlorine in the lower atmospheric layer takes place as the result of oxidation of the sea salt particles. The chlorine excess is discovered in the free atmosphere later on. This process is confirmed by the presence of gaseous chlorine as HCl detected by JUNGE (1957) as well as by increase of the ratio Cl′/Na· in the precipitation collected at the mountain stations (E. ERIKSSON, 1958).

The results of cloud water analysis also show

TABLE 2. *The chemical composition of cloud water samples in the south-west of ETU from different clouds.*

Cloud form	Concentration mg/l									pH	$\lambda \cdot 10^6$ Ω^{-1} cm^{-1}	Total	Cl′/Na·	SO_4''/Cl′	No. of samples
	SO_4''	Cl′	NO_3'	HCO_3'	$NH_4^·$	Na·	K·	Mg··	Ca··						
St, Sc	11.4	2.2	1.0	0.01	2.4	0.7	0.7	0.5	0.9	4.5	53	19.8	3.1	5.2	27
Ns	5.3	2.0	0.4	1.1	0.9	0.7	0.5	0.4	1.0	5.2	21	12.2	3.0	2.6	19

a high value of the ratio Cl′/Na·. Perhaps there are some other mechanisms explaining this increase. In particular in the south-west of ETU where the ratio Cl′/Na· is 3.1 it is obviously accounted for by the gaseous chlorine injected into the atmosphere by industrial sources.

It should be noted that Table 1 contains the mean values giving a general representation of the composition of precipitation and cloud water; the data on the chemical precipitation composition have been obtained on the basis of averaging of four-year observations (V. M. DROZDOVA, O. P. PETRENCHUK, E. S. SELEZNEVA & P. F. SVISTOV, 1964); the data on cloud water for different regions have been averaged without taking into account the cloud form and the sampling height.

At a more detailed examination it is discovered that cloud water composition varies for the different cloud forms. It follows from obtained data that samples taken from the clouds St, Sc have more high concentration of almost all constituents in comparison with the clouds Ns (Table 2).

Since the small droplets in the clouds type of St, Sc predominate as compared to the clouds Ns, one can suppose that in the St, Sc the cloud droplets are a very concentrated solution of the soluble condensation nuclei. In the clouds St, Sc Shmeter has also obtained the higher concentration than that of the frontal clouds type Ns-As.

The question about the dependence of constituent concentration in the cloud droplet size is closely connected with one of the important problems of the physics of clouds and precipitation, namely with the clearing up of the growth mechanism of cloud droplets. The investigations by TURNER (1955) and SPENCER & WOODCOCK (1963) showed that the raindrop salinity is the function of their radius which is different for the raindrops falling from warm or supercooled clouds. In a supercooled cloud the condensation mechanism of growth predominates and the salinity of falling raindrops may be expressed as $C \sim r^n$ where n is a positive value dependent of the cloud base height. For the warm clouds that dependence is disturbed and the largest falling drops have a high salinity alongside with small raindrops. According to this Spencer & Woodcock suggested that the largest cloud drops form on giant salt nuclei and then increase by coagulation with one another.

TURNER (1955) obtained the interesting data on salinity of raindrops against the collection height as regards the cloud base. However, these results related only to the raindrops. For the explanation of the mechanism of cloud drop growth it is important to investigate the chemical cloud water composition in connection with droplet size.

Of great interest is the study of the cloud water composition against the height of its sampling. There are different opinions on the question. For example, ODDIE (1962) when investigating the results of analysis of cloud water collected in environs of London discovered the concentration of constituents in cloud water to decrease with height. According to Grabovsky's data such dependence does not exist. He noted even some increase of chloride to the upper part of cloud, though the thickness of the cloud layer was small and merely amounted to 200–300 meters.

In our case the cloud water sampling had been carried out at the different heights. The analysis of data obtained shows that on the whole there is no simple connection between the height of sample collection and their chemical composition. Only for heavily polluted samples taken from the subinversion clouds in industrial regions can one see a sharp decrease

TABLE 3. *Chemical composition of the most contaminated cloud water samples.*

No.	Location	Date	Cloud form	Height (m)	Concentration mg/liter SO_4''	Cl'	NO_3'	NH_4^+	Na^+	K^+	Mg^{++}	Ca^{++}
1	Kiev	3 Dec.	St, Sc	550	91.50	7.76	12.20	24.60	1.80	4.80	—	10.70
2	Kiev	3 Dec.	St, Sc	850	91.50	6.80	10.60	13.00	1.82	1.81	0.48	2.58
3	Kiev	3 Dec.	St, Sc	900	45.50	4.04	4.80	10.70	1.21	0.21	0.29	1.53
4	Kiev	5 Dec.	St, Sc	550	99.00	11.48	4.90	28.70	5.00	2.20	1.90	3.70
5	Kiev	5 Dec.	St, Sc	1000	40.50	6.80	4.00	11.90	1.45	5.02	0.43	0.83
6	Dnepropetrovsk	7 Dec.	St	500	157.50	42.17	6.50	28.70	7.60	10.00	5.60	40.00
7	Dnepropetrovsk	7 Dec.	St	1200	20.70	8.40	1.04	5.00	1.96	2.53	0.29	0.87
8	Odessa	7 Dec.	St	900	94.00	4.18	4.80	12.20	2.20	3.40	1.50	12.60
9	Kiev	7 Dec.	St	1250	19.00	5.17	1.06	4.20	1.83	3.05	0.20	1.91

Continued.

No.	Concentration mg-equiv./liter SO_4''	Cl'	NO_3'	NH_4^+	Na^+	K^+	Mg^{++}	Ca^{++}	H^+	pH	$\lambda \cdot 10^6$ Ω^{-1} cm^{-1}	Sum of ions	Sum of anions	Sum of cations	Diff.
1	1.877	0.220	0.197	1.305	0.078	0.122	—	0.535	0.110	3.96	294	153.36	2.294	2.211	0.083
2	1.877	0.192	0.171	0.722	0.079	0.046	0.040	0.129	0.447	3.35	268	128.59	2.240	1.463	0.777
3	0.948	0.115	0.077	0.593	0.052	0.031	0.024	0.076	0.200	3.70	171	69.27	1.140	0.976	0.164
4	2.062	0.325	0.079	1.159	0.216	0.056	0.158	0.185	0.004	5.40	252	156.88	2.466	1.778	0.664
5	0.844	0.192	0.065	0.662	0.063	0.129	0.036	0.041	0.229	3.64	221	70.93	1.101	1.160	−0.059
6	3.281	1.191	0.105	1.600	0.331	0.256	0.467	2.000	0.003	5.46	483	298.07	4.577	4.654	−0.077
7	0.431	0.237	0.017	0.277	0.085	0.065	0.024	0.043	0.022	4.65	77	40.79	0.685	0.516	0.169
8	1.958	0.119	0.077	0.680	0.096	0.110	0.123	0.629	0.001	5.90	218	135.78	2.154	1.639	0.515
9	0.396	0.147	0.017	0.233	0.079	0.078	0.016	0.095	0.026	4.58	79	36.42	0.560	0.527	0.033

of the constituent concentrations with height (Table 3).

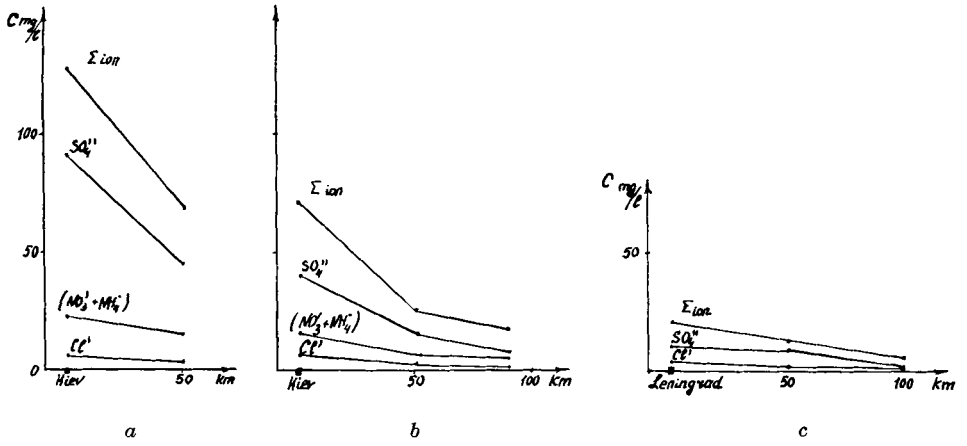
The cloud water composition is affected remarkably by the atmospheric pollution in industrial regions. This can be concluded from the consideration of successive samples collected from the clouds at different distances from the city.

Fig. 1 shows the change of some constituent concentrations and total ion amount in the cloud water samples taken not far from Leningrad and Kiev. Approaching the city the total mineralization as well as the concentration of some constituents (SO_4'', Cl', NO_3') sharply increases.

The influence of cities can be also observed on example of the flight carried out on the 7th of December, 1963, on the route Dnepropetrovsk–Odessa–Kiev. The changes of total ion amount of samples collected along the route are presented in Fig. 2. The sharp increase of total mineralization of samples collected directly over the city has also been observed here. For instance, the total mineralization of cloud water sample is 280 milligrams per liter over Dnepropetrovsk. It is interesting that such great values are unusual not only for the cloud water but also for the precipitation. The investigation of chemical precipitation composition has shown the maximum frequency of total mineralization in it to be only 20–30 milligrams per liter (DROZDOVA *et al.*, 1964).

From the examples presented one may attribute to the clouds an important role in the process of atmospheric refinement. This agrees well with STYRO's investigations (1959) considering clouds as an important factor in atmospheric self-refinement from radioactive contamination.

Industrial sources and large cities influence



a b c

FIG. 1. The change of some ion concentration and total ion amount at different distances from the city; (*a*) 3.12.63, $H_{sampl.}$ 850 m; (*b*) 5.12.63, $H_{sampl.}$ = 1000–1200 m; (*c*) 6.12.63, $H_{sampl.}$ = 900 m.

aerosol content in the free atmosphere. SELEZNEVA (1963, 1964) published the concentration data of condensation nuclei obtained by the Sholz counter in the free atmosphere. The condensation nuclei have been measured during horizontal flights over different regions. Approaching an industrial center or a large city during these flights a sharp peak of condensation nuclei which remains sometimes up to a height of 2000 or 3000 meters is observed.

Unusually large total ion amount of cloud water samples in south-west ETU (from the 3rd to the 7th of December) is accounted by the existence of spacious stationary anticyclon with sharp temperature inversion during the collection time, the samples being taken from subinversion clouds. An example of temperature change with height is given in Fig. 3.

The most polluted cloud water samples collected during this period of time have been combined in a separate group. Their chemical composition is represented in Table 3. The constituent concentration in the samples is expressed in milligrams per liter and for convenience of further calculations and analysis control in milligram-equivalent per liter. From

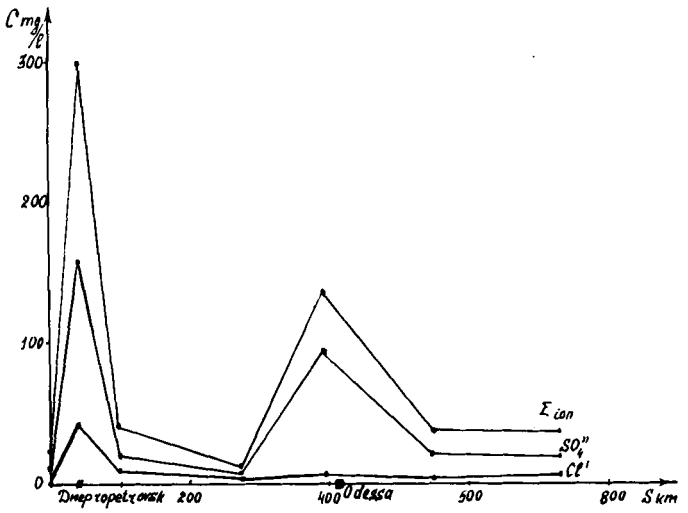


FIG. 2. The change of some ion concentration and total ion amount during the route flight.

Table 3 one may see the apparent above-mentioned dependence of constituent concentration with height.

In addition to a high content of soluble constituents there was a considerable amount of insoluble constituents in most samples examined. It had been discovered after thorough elaboration of polluted samples and spectral analysis of obtained sediment that it contains copper, iron, beryllium, vanadium, cobalt, chromium, molybdenum, manganese, aluminum, zinc, nickel, silicon.

It is characteristic that in heavily contaminated samples the anion sum in terms of equivalent weights exceeds in the main that of cation. It may be apparently explained by the presence in them of elements not determined usually by analysis and discovered in particular on spectrograms. Let us note that ODDIE 1962 had also obtained on the average excess of anions as compared to the cations for the polluted samples.

Consideration of Table 3 shows most samples to be acid and to have a low pH value (sometimes pH lower than 4). According to this a high concentration of hydrogen ions is found. There is as a rule a large concentration of SO_4'', Cl', NO_3' in samples with high total ion amount. Since in most cases concentration of the ions exceeds considerably the cation sum (without hydrogen ions), in terms of equivalent weights, one may suppose that they exist in the cloud water samples as acids. The presence of hydrochloric acid in the water may result in an essential increase of the ratio Cl'/Na' which is observed in reality particularly in industrial regions.

On the basis of the investigation carried out one can draw the following conclusions.

Although on the average the total ion amount of cloud water is slightly different from that of atmosphere precipitation there is a remarkable difference in their chemical composition.

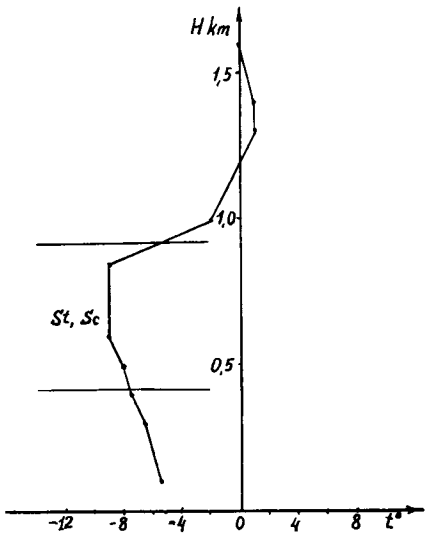


FIG. 3. The change of temperature with height (Kiev, 3.12.63).

The results obtained show that subinversion clouds even not precipitated are peculiar filters capturing different contaminations from the atmosphere and stimulating its refinement to some extent.

Acknowledgments

The authors are indebted to the Laboratory chief E. S. Selezneva for valuable advice and comments on their work. The authors would like to thank collaborators M. A. Beljashova and V. G. Ivanova who took part in flights. Thanks are also due to the pilots G. S. Danilov, V. E. Maslennikov, V. S. Pavlov and V. V. Podjachy who accomplished the flight programme.

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О ХИМИЧЕСКИХ СОЕДИНЕНИЯХ СОДЕРЖАЩИХСЯ В ВОДЕ ОБЛАКОВ

В статье рассмотрены химические соединения содержающиеся в воде облаков, собранной в различных областях СССР. На основании их анализа и дальнейшего обобщения получены главные характеристики химических примесей. Хотя полное число ионов в облачной воде мало отличается от числа ионов в дождевой, химические соединения различны. Должно быть также отмечено большое влияние на химические соединения в воде облаков промышленного загрязнения воздуха.