

On the variation of the size distribution of large and giant atmospheric particles as a function of the relative humidity

By ÁGNES MÉSZÁROS, *Institute for Atmospheric Physics¹ Budapest, Hungary*

(Manuscript received February 26, 1971; revised version June 7, 1971)

ABSTRACT

Atmospheric aerosol samples captured by a cascade impactor were examined under a microscope at different relative humidities to gain some informations on the variation of the size distribution of large and giant particles as a function of the relative humidity. The results of ten samplings are presented and discussed.

I. Introduction

The investigation of water-soluble substances in atmospheric aerosols is of interest for many problems in air chemistry, cloud physics, atmospheric optics and air pollution. It is well known that the water-soluble particles change phase and grow by condensation well below the saturation level, which results in a variation of the size distribution as a function of the quantity and chemical nature of hygroscopic materials.

The growth of water-soluble particles formed artificially in the laboratory was studied in detail by Dessens (1949) and mainly by Orr et al. (1958). Experiments with natural aerosols were made by Dessens (1949) and Junge (1952) who investigated with a microscope individual particles captured on spider web. This latter author also studied the ratio of the concentration of atmospheric particles collected at different humidities on impactor slides covered partly by sticky, partly by non-sticky materials to separate dry particles and droplets. Furthermore, the variation of the total mass of atmospheric aerosols captured by an impactor was determined more recently by Winkler (1969).

The variation of the size distribution of atmospheric particles can also be investigated in an indirect way by measuring at different humidities the optical properties of the atmos-

phere. An interesting paper on this subject was published by Rosenberg (1967) according to which particle growth can be observed in some situations even in the surroundings of 30% relative humidity.

The aim of this paper is to present the results of direct measurements of the variation of the size distribution of large and giant atmospheric particles as a function of the relative humidity.

2. Experimental

The samples of atmospheric particles were taken by a Casella cascade impactor. During the samplings only three stages were operated, the jet widths of which are: ~ 6.5 mm, 1.45 mm and 0.27 mm. A suction rate of 50 l/min was used. The collection efficiencies of different jets were determined according to May (1945) who measured experimentally the efficiency of rectangular jets as a function of the so-called inertia parameter. In the course of the calculation spherical particles with the density 1.5 g/cm^3 were supposed. It was demonstrated by this calculation that the last stage of the sampler collects with a 100% efficiency all particles having a radius equal to or larger than 0.15μ . Thus, using an optical microscope, the concentrations can be determined without any correction.

The particles were collected on cover glasses coated with a sort of polystyrene dissolved in 1,2-dichloroethane. This coating is transparent

¹ Formerly Main Aerological Observatory.

and its surface is solid to prevent particle penetration. The contact angle of liquid water on this substrate is 90° . The effect of particle loss which can occur because of this non-sticky collection surface was studied by comparing the impactor concentrations with those measured by membrane filters. Practically no difference was found even below 64% relative humidity.

For making air with known relative humidity the isopiestic method was applied. The principle of this method is as follows: over the saturated solutions of given salts in water a known relative humidity forms. The isopiestic method was first used by Woodcock (1952) to identify sea-salt particles, while the critical examination of the procedure was made by Toba (1966). In our case the solution was poured in a small cylindrical plexi-glass box with a diameter of 15 mm. The height of the box was 5 mm. This box was covered by the collecting slide (cover glass) in such a way that the sample faced downwards. The distance between the sample and solution surface was about 2 mm. The box prepared in this way was placed under an optical microscope to count and size the collected particles.

The examination of samples was carried out at five different humidities. The saturated solutions of the following salts were used: $(\text{NH}_4)\text{NO}_3$, NaCl, KCl and $\text{Pb}(\text{CNO})_2$, which give at an approximate temperature of 20°C the following humidities: 64%, 76%, 86% and 98% (O'Brien, 1948). The first humidity step was produced by dry P_2O_5 , which created, according to the measurements, about 20% relative humidity. During the microscopic manipulations, which were made by increasing the humidity, the illuminating light was transmitted through a water bath with a thickness of 5 cm to trap the heat. It is to be noted here that no heat isolation was applied around the boxes. But the temperature of the laboratory where microscopic examinations were made was always $20\text{--}22^\circ\text{C}$.

The concentration and size distribution of dry particles and droplets were determined on the three stages of the impactor at the five humidities mentioned above. All particles, the surface of which was partly or entirely covered by liquid, were considered as droplets (mixed particles). The sizing and counting were made for particles of $r \geq 0.2 \mu\text{m}$. It is to be noted, however, that the discrimination of dry particles

and droplets was rather uncertain below $0.5 \mu\text{m}$ radius, but for the sake of completeness the data concerning particles of $0.2 < r < 0.5 \mu\text{m}$ are also presented. The real size of droplets was determined from the radius of the half-sphere, measured under the microscope, by means of the following formula:

$$r(\text{droplet}) = \frac{1}{\sqrt{2}} r(\text{measured})$$

3. Results

Ten samplings were carried out in the garden of the Institute for Atmospheric Physics (in the outskirts of Budapest) in the period from January to July, 1970. Five out of ten measurements were made in the winter, while the others were carried out in the summer half-year. Table I shows the sampling dates and times, the sampling conditions as well as the total concentrations of particles with $r \geq 0.2 \mu\text{m}$ measured at 20% relative humidity. It can be seen that all samplings were executed when the relative humidity of the atmosphere was below 64%. There is practically no difference between mean relative humidities for the summer and winter half-year. The winter samples were taken in more polluted air as indicated by larger particle concentrations.

Fig. 1a and 1b give, for the winter and summer half-year, the average size distribution of dry particles (solid lines) and droplets (dotted lines). It is seen that droplets can be observed even at 20% relative humidity. The number of

Table 1. *Details and particle concentrations at 20% relative humidity of individual samples*

Date	T[$^\circ\text{C}$]	RH[%]	N[cm^{-3}]
<i>Winter</i>			
28.01.1970 13 h	4.9	64	270
16.02.1970 12 h	-2.0	58	360
19.02.1970 12 h	0.2	65	400
25.02.1970 13 h	1.8	62	227
04.03.1970 12 h	4.8	60	155
Average	1.9	62	282
<i>Summer</i>			
21.05.1970 13 h	19.6	48	106
09.06.1970 13 h	25.4	63	93
18.06.1970 13 h	20.0	62	188
22.07.1970 12 h	26.9	50	191
29.07.1970 12 h	25.8	45	194
Average	23.5	54	154

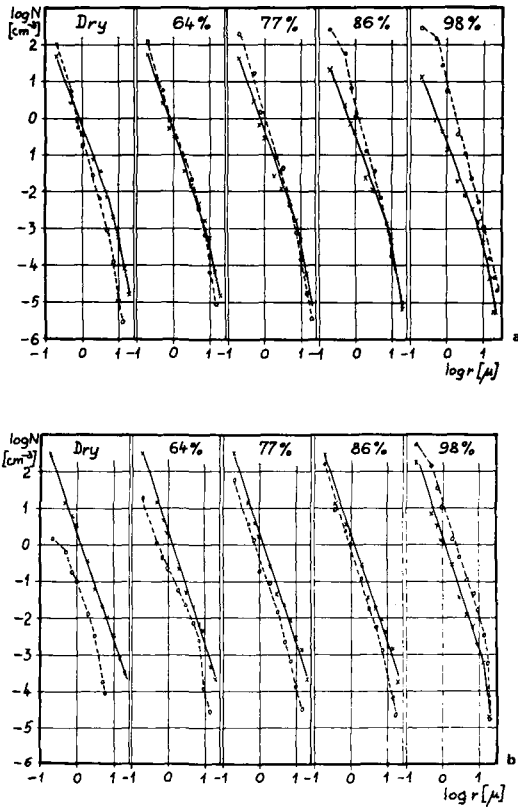


Fig. 1. Size distribution of dry particles (—) and droplets (---) as a function of the relative humidity of the air. N gives the concentration of particles with radius larger than r . (a) Winter; (b) Summer.

droplets at this humidity is particularly high in the summer. One can suppose that these droplets consist of either supersaturated salt or concentrated acid solutions. The number of droplets gradually grows with the increase in relative humidity. In the whole size range ($r \geq 0.2 \mu\text{m}$) the $N_{\text{droplet}}/N_{\text{total}}$ ratio (where N is the concentration) is given in Table II for different humidities. Our summer figures are in rather good agreement, except at 20%, with Junge's results (Junge, 1952) obtained in Frankfurt in the summer of 1950 by means of a method mentioned in the introduction.

Fig. 2 represents the $N_{\text{droplet}}/N_{\text{total}}$ ratios as a function of the size of the particles in the winter and summer samples. One can see that this ratio decreases with increasing particle size. Supposing that the number of droplets is unambiguously related to the quantity of water-

Table 2. $N_{\text{droplet}}/N_{\text{total}}$ ratio of large and giant aerosol particles as a function of the relative humidity in the winter and summer half-years

Rel. hum. (%)	20	64	76	86	98
Winter	0.005	0.054	0.16	0.32	0.73
Summer	0.67	0.69	0.83	0.92	0.96

soluble materials it can be estimated that there is a strong correlation between the quantity of these substances and the size of the particles. This statement is in agreement with the results of our chemical measurements made with the aim of estimating the size distribution of the mass-concentration of water-soluble materials (E. Mészáros, 1968).

Fig. 3 shows the common distribution of dry particles and droplets at different humidities for the summer and winter. In this figure only the $r \geq 0.5 \mu\text{m}$ size range is considered because one can suppose that this size limit is not reached by dry particles having a radius smaller than $0.15 \mu\text{m}$ for which the collection efficiency is unknown and smaller than unity. It follows from this figure that in the summer the variation of the size distribution of larger atmospheric particles is more gradual than in the winter. In the latter season the size of the particles changes essentially only between 86% and 98%.

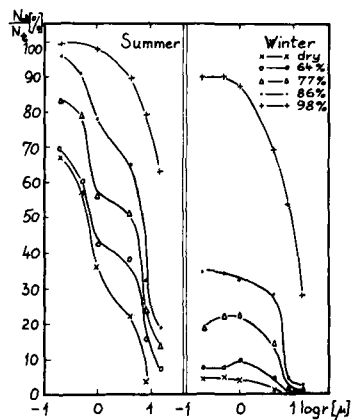


Fig. 2. Ratios of the concentration of droplets (N_d) to that of all particles (N_t) as a function of the particle size.

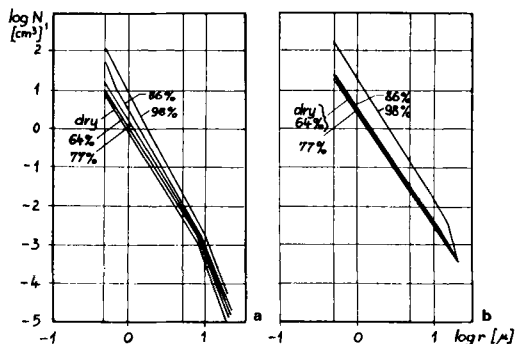


Fig. 3. Size distribution of all particles as a function of the relative humidity. (a) Summer; (b) Winter.

According to Fig. 3 the individual growth of particles of different sizes can be estimated as a function of the relative humidity. For this estimation it is necessary to presume that particles having the same size grow in a similar way. Fig. 4a and 4b give for the winter and summer half-year the growth of particles of different radius referred to the dry size. It can be seen that with increasing particle size the measure of the particle growth decreases. Our results for 0.5 μ radius are in good agreement with those of Hänel (1970) who calculated theoretically the growth of the particle size with increasing relative humidity according to the measurements of Winkler (1969) mentioned in the introduction. It is to be noted, however, that Hänel's results do not show any variation of this ratio as a function of the particle size.

The connection between the relative growth and particle size can be explained by the fact that the quantity of droplets (or water-soluble materials) increases with decreasing particle radius. On the other hand, according to the measurements, in the giant size range practically all water-soluble substances are on mixed particles, the material of which is mostly insoluble in water. In a large part of these mixed particles the insoluble substance is not entirely wettable with liquid water.

4. Discussion

An interesting result of this study is the fact that there is a seasonal difference in particle growth. As was mentioned above (Fig. 3), in summer the growth of particles with increasing

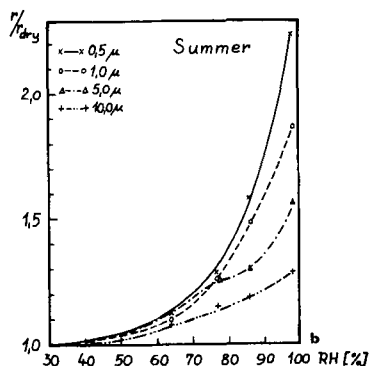
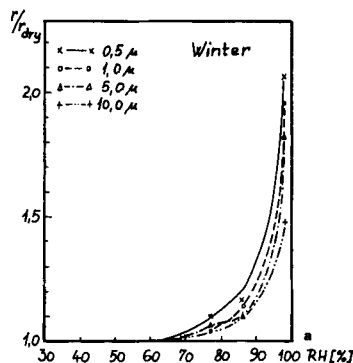


Fig. 4. Relative growth of particles of different sizes as a function of the relative humidity. (a) Winter; (b) summer.

humidity is more gradual than in winter. In the latter half-year there is some water-soluble substance in the particles, which changes phase above 86 %.

It is very difficult to explain the difference between the winter and summer half-years. It seems possible, however, that the probability of the presence of either supersaturated solution droplets or some acid particles is greater in the summer. This fact probably causes an important seasonal difference in the variation of visibility with humidity.

Finally, some cloud physical considerations may be made. Some years ago the concentration and size distribution of fog drops were measured in the garden of our institute by a cascade impactor of two stages. The drops were captured on glass slides covered by pure gelatine. This technique made possible the counting and sizing of drops with radius larger than about 1 μm. It was shown by these measure-

ments that in freshly formed winter radiation fog the average drop concentration is 20 cm^{-3} (A. Mészáros, 1965). It follows from Fig. 1a of the present paper that at 98% relative humidity, droplets of radius equal to and larger than $0.8 \mu\text{m}$ have the same concentration. It seems evident that fog drops formed from these largest droplets. By assuming that droplets measured in this program are composed of ammonium sulfate solution it is a simple matter to calculate

the dry radius of active fog nuclei by means of the thermodynamic formula (E. Mészáros, 1969) giving the connection between relative humidity and equilibrium droplet radius. The calculation shows that a solution droplet having a radius of $0.8 \mu\text{m}$ at 98% relative humidity contains such a quantity of ammonium sulfate ($T = 0^\circ\text{C}$) the dry radius of which is about $0.34 \mu\text{m}$. This means that active fog nuclei were larger than this value.

REFERENCES

- Dessens, H. 1949. The use of spiders' threads in the study of condensation nuclei. *Quart. J. Roy. Meteor. Soc.* 75, 23-27.
- Hänel, G. 1970. Die Grösse atmosphärischer Aerosolteilchen als Funktion der relativen Luftfeuchtigkeit. *Beit. Phys. Atmos.* 43, 119-132.
- Junge, Ch. 1952. Die Konstitution des atmosphärischen Aerosols. *Annal. Meteor.* 1952, 1-55.
- May, K. R. 1945. The cascade impactor: an instrument for sampling coarse aerosols. *J. Sci. Instr.* 22, 187-195.
- Mészáros, A. 1965. Concentration et distribution dimensionnelle des gouttelettes de brouillards atmosphériques. *J. Rech. Atm.* 2, 53-64.
- Mészáros, E. 1968. On the size distribution of water soluble particles in the atmosphere. *Tellus* 20, 443-448.
- Mészáros, E. 1969. On the thermodynamics of the condensation on water-soluble and mixed nuclei. *Időjárás.* 73, 1-11.
- O'Brien, M. A. 1948. The control of humidity by saturated salt solutions. *J. Sci. Instr.* 25, 73-76.
- Orr, C., Hurd, F. K., Corbett, W. J. 1958. Aerosol size and relative humidity. *J. Colloid Sci.* 13, 472-482.
- Rosenberg, G. V. 1967. Properties of atmospheric aerosols according to optical measurements (in Russian). *Fizika Atmosf. Okeana* 3, 936-949.
- Toba, Y. 1966. Critical examination of the isopiestic method for the measurement of sea-salt nuclei masses. *Special Contr., Geophys. Inst., Kyoto Univ.* 6, 59-67.
- Winkler, P. 1969. Untersuchungen über das Grössenwachstum natürlicher Aerosolteilchen mit der relativen Feuchte nach einer Wägemethode. *Annal. Meteor.* (Neue Folge) 4, 134-137.
- Woodcock, A. H. 1952. Atmospheric salt particles and rain drops. *J. Meteor.* 9, 200-212.

О ВАРИАЦИЯХ РАСПРЕДЕЛЕНИЯ ПО РАЗМЕРАМ БОЛЬШИХ И ГИГАНТСКИХ АТМОСФЕРНЫХ ЧАСТИЦ В ЗАВИСИМОСТИ ОТ ОТНОСИТЕЛЬНОЙ ВЛАЖНОСТИ

Пробы атмосферного аэрозоля, собранные при различных относительных влажностях с помощью каскадной ловушки, были исследованы под микроскопом с целью получения ин-

формации об изменениях распределения больших и гигантских частиц как функции относительной влажности. Представлены и обобщены результаты 10 проб.