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Studies on atmospheric particulate matter at Delhi

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ABSTRACT. Making use of a simple technique, a study has been made on a number of days, spread over a period of 20 months during 1960-62, of the concentration of nitrate, chloride and sulphate particles in the atmosphere in ground air layers at Delhi. In general, nitrates or nitrate containing other salts (mixed nuclei) are found to predominate over both chlorides and sulphates. All the three components appear to have a common origin which is, perhaps, the sea. The concentrations are seen to decrease by about two orders of magnitude during winter and summer as compared to the monsoon season.

1. Introduction

It is generally accepted that giant hygroscopic particles in the atmosphere play a vital role in the growth of precipitation from warm clouds. The ability of such particles to start the rain mechanism depends on their chemical composition and on their size. Studies made earlier at Delhi (Ramana Murty *et al.* 1962) on the concentration of giant hygroscopic particles revealed many important features, as for example, the dependence of their concentration on airmass characteristics and on the scavenging effect of rain. On account of certain considerations, such as, the observed increase in particle number with incursion of moist air into the area, it was suggested that the giant hygroscopic nuclei found in the surface air at Delhi were largely sea salt particles. No further attempt was made at that time to go into their chemical nature. In this paper, we present the results of an investigation on the chemical composition of aerosols. We have confined our study to three major components, namely, chlorides, sulphates and nitrates of the giant hygroscopic nuclei found in the surface air over Delhi.

2. Equipment and method

As in the previous study, the Cascade Impactor (May 1945), consisting of a system of 4 jets and sampling slides in series, was used for collecting samples of atmospheric particulate matter. Clean glass slides without any adhesives were used, although this meant losing a small portion of the smaller particles. A known volume of air was drawn through the Impactor by means of a suction pump of known capacity (16 litres/minute). As it is the property of all hygroscopic particles to pass into solution at different humidities depending on their chemical composition (Twomey 1953), a simple method was derived from this criterion. The glass slide, with a deposit of aerosols on it, was examined under different known humidities, and the size distribution of droplets formed was measured under a high power microscope. From information on the phase transition of various salts, which is available from a number of standard works, it was possible to make a reasonable guess about the presence of chlorides, sulphates and nitrates.

The five different relative humidities, at which counts were made, were 43, 67, 80, 91 and ~ 100 per cent respectively. The humid environment was created by employing saturated aqueous solutions of potassium carbonate, sodium nitrate, ammonium chloride, sodium sulphate and distilled water

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TABLE 1*

Different compounds showing phase transition at specified humidities

Name of compound	Relative humidity (in percentage) at the point of phase transition	Temperature (in°C) at transition point
$NaCl+KNO_3+NaNO_3$	13·5	16·4
$CaCl_2 \cdot 6H_2O$	32·3	20·0
$NaCl + KNO_3$	32·6	16·4
$Ca\ (NO_3)_2 \cdot 4H_2O$	51	24·5
$NaHSO_4.H_2O$	52	20·0
$Mg\ (NO_3)_2 \cdot 6H_2O$	56	18·5
$NH_4Cl\ +KNO_3$	72·6	20·0
$NaClO_3$	75	30·0
NH_4Cl	79·2	20·0
$(NH_4)_2SO_4$	81	20·0
$KHSO_4$	86	20·0
$(Na)_2SO_4 \cdot 10H_2O$	93	20·0
K_2SO_4	97	20·0

*The data mentioned in the table except for one compound, namely, K_2SO_4, are taken from the *Hand Book of Chemistry and Physics*, published by the Chemical Rubber Publishing Co., Cleveland, Ohio. The values for K_2SO_4 are as given by Twomey (1953), *J. appl. Phys.*, **24**, 9, p. 1100.

in a closed space. A small quantity of the solution was put in a separate perspex container, each meant for one particular humidity. The perspex container was specially made with provision to hold a glass slide well above the solution surface at the bottom. The slide, with the exposed surface upwards, was placed inside the chamber, which was then closed at the top with a transparent cover. Within a few minutes the hygroscopic particles on the strip came into equilibrium with the humidity inside the chamber. This was then transferred to the stage of a microscope. The entire strip of deposit on the slide was scanned, and all the solution droplets were measured with the help of a graticule fitted on the eyepiece of a microscope. The operations were repeated at progressively increasing relative humidities. The sample deposited only on one particular slide (No. 2) was analysed because the bulk of the atmospheric particulate matter, which could initiate a chain reaction by the the coalescence process, were collected on that slide.

The measurements of size have been grouped under three categories, A, B and C depending on whether the diameter of the drop, which assumes the shape of a plano-convex lens, is less than half, is less than one or less than one and half graticule division (one graticule division is 22·5 microns) respectively. From Table 1, in which we have listed some of the compounds known to undergo phase transition, it is seen that all nuclei forming liquid drops below 67 per cent, between 67 and 80 per cent and between 80 per cent and complete saturation may be considered as being composed of nitrates, chlorides and sulphates respectively.

The probable sizes of dry particles forming droplets at different humidities under group A, group B and group C have been calculated from the growth equation of Wright (1936) as considered by Best (1957). These are given in Table 2. While calculating the sizes, an average flattening correction of 0·75 (May 1945) was used for converting the measured diameters of the observed droplets, so that they correspond to spherical droplets of equal volume. In the same table, we have also shown the sizes likely to be attained by droplets formed on the dry particles after they have remained inside a cloud for 10 minutes, assuming that the relative humidity within the clouds is 100 per cent. These values have been obtained from the computations of Keith and Aarons (1954). While preparing this table, ϕ factors (*vide* Appendix) 8·8, 6·0 and 13·0 and densities 2·267, 2·06 and 1·77 were used for particles showing phase transition below 67 per cent, between 67 and 80 per cent and between 80 per cent and water saturation respectively. These values are applicable to $NaNO_3$, sea salt (NaCl) and $(NH_4)_2SO_4$. We note from this table that the particles showing phase transition at all humidities and under all groups, except those at ~ 100 per cent under group A, could be treated as giant

TABLE 2

R. H.	Mass and size of dry particles before going into solution						Radius of the drop formed after particles have remained for 10 minutes under 100 per cent R. H.		
	Group A		Group B		Group C		Group A	Group B	Group C
(%)	mass (μμg)	radius (μ)	mass (μμg)	radius (μ)	mass (μμg)	radius (μ)	(μ)	(μ)	(μ)
44	46·3	1·70	1250·3	5·09	5787·6	8·48	17·4	34·7	47·8
67	27·3	1·42	736·9	4·27	3411·0	7·11	15·5	31·0	39·2
80	11·3	1·09	304·6	3·28	1409·8	5·47	12·9	25·8	38·5
91	11·0	1·14	297·3	3·42	1375·3	5·66	12·9	25·7	38·5
~100*	1·3	0·56	33·5	1·65	154·1	2·75	8·2	16·1	22·4

*For the purpose of calculation, this humidity is taken as 99 per cent

TABLE 3

Monthly mean concentrations (number per litre and also percentage concentrations) of nitrates, chlorides and sulphates in ground air layers at Delhi during 1960-62

	Nitrates		Chlorides		Sulphates		No. of days on which observation made
	Mean concentration	Percentage concentration	Mean concentration	Percentage concentration	Mean concentration	Percentage concentration	
Jan	0·23	44	0·07	16	0·23	40	23
Feb	0·08	26	0·09	25	0·14	49	21
Mar	0·10	22	0·15	42	0·18	36	2
Apr	0·91	46	0·35	30	0·23	24	8
May	0·29	35	0·20	30	0·33	35	24
Jun	3·16	46	2·62	32	1·87	22	5
Jul	16·10	49	4·30	22	12·30	29	12
Aug	5·27	46	0·74	24	1·08	30	12
Sep	2·02	53	0·43	14	0·56	33	12
Oct	0·56	53	0·21	21	0·26	26	13
Nov	0·19	49	0·09	26	0·11	25	24
Dec	0·24	47	0·07	20	0·11	33	28

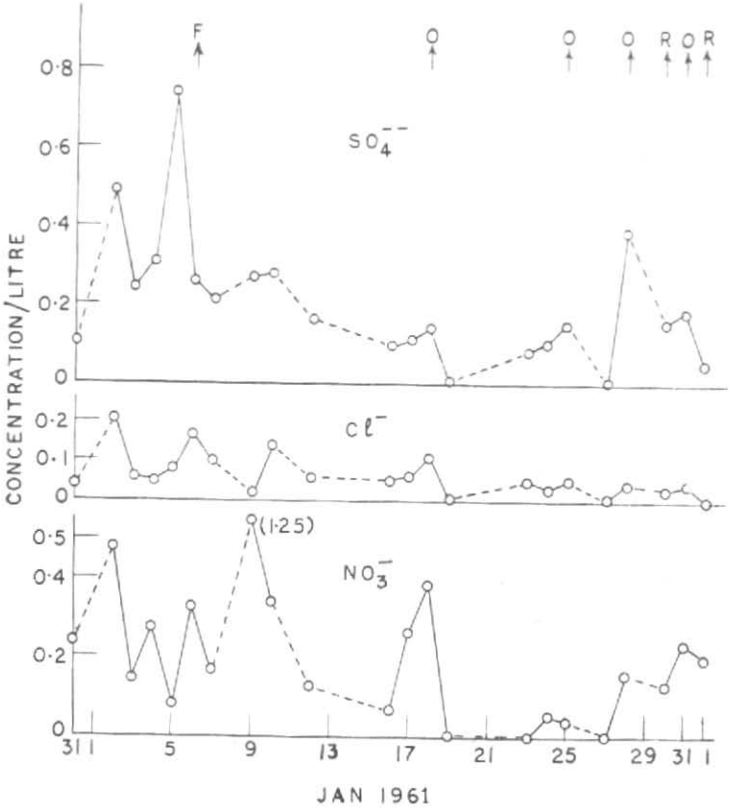

Fig. 1(a). Daily variation in concentration (number per litre) of nitrate, chloride and sulphate particles in the atmosphere at Delhi

F—Fog, O—Overcast, R—Rain

hygroscopic nuclei suitable for initiating rain from clouds.

3. Results

(a) *Monthly variations*

From observations available over a period of 20 months during 1960-62, the actual mean monthly concentrations (number of particles per litre of air sampled) of nitrates, chlorides and sulphates and also their mean monthly percentage concentrations have been calculated and shown in Table 3 (p. 203). The total number of days on which measurements were made in each month is given in the last column of the table.

It is seen from the data that the major portion of the particulate matter in the atmosphere is nitrate in nature. Sulphates appear to occupy the second place while chlorides, the third. The concentration of all the three components start showing a marked increase from June, and reach their maximum value after the monsoon has set in, *i.e.*, during July. The lowest values are reached in February (for nitrates) and December (for both chlorides and sulphates). However, as far as the maximum and minimum percentage concentrations are concerned, these are reached in different months. Maximum percentage for nitrates is reached during the monsoon period, for chlorides during the pre-monsoon period and for sulphates during winter. The nitrate, chloride and sulphate minima (percentage) were recorded during February, September and June respectively. Even during important periods of weather, *i.e.*, during the southwest

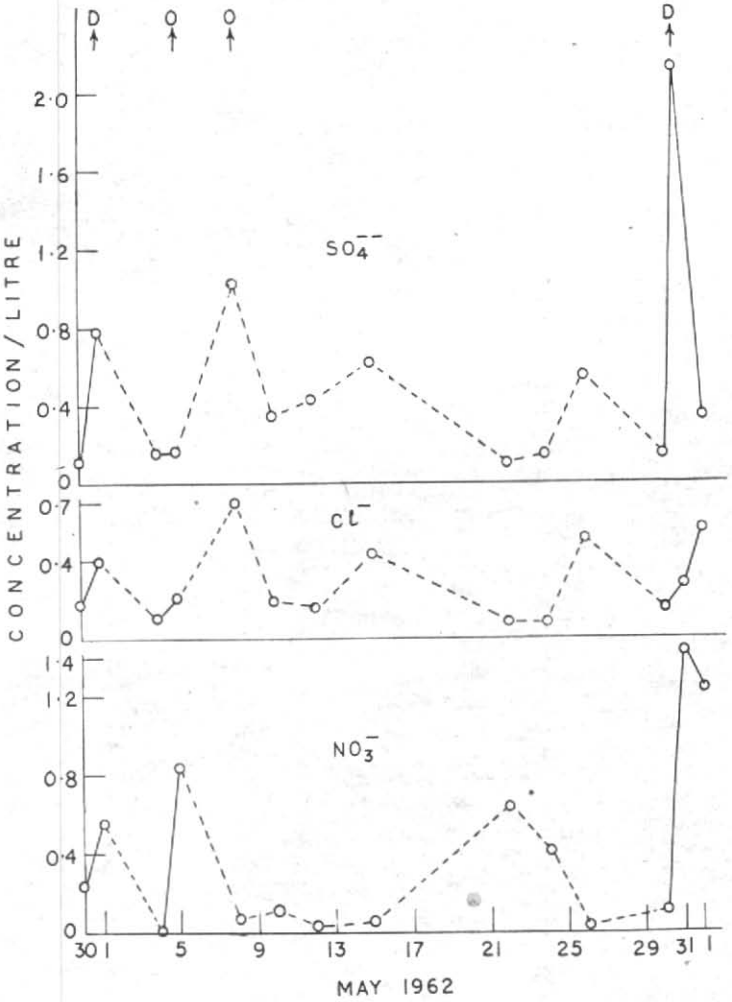

Fig. 1(b). Daily variation in concentration (number per litre) of nitrate, chloride and sulphate particles in the atmosphere at Delhi

O—Overcast, D—Duststorm

monsoon, nitrates and sulphates predominate over chlorides.

The manner in which these three groups of atmospheric particles vary in their content from day-to-day during mid-summer, mid-monsoon and mid-winter has been shown in Figs. 1(a) to 1(c). It is found that these three major constituents in the atmosphere undergo, in general, a similar type of variation in their concentrations. Although there is no one to one correspondence, it is usually seen that if one constituent decreases or increases the other two also may decrease or increase. This feature suggests that the possible source for nitrates, chlorides and sulphates is, perhaps, one and the same.

Also, it is seen that on some exceptional days most of the particulate matter present in the atmosphere belonged to either one or the other of the three categories, *i.e.*, either

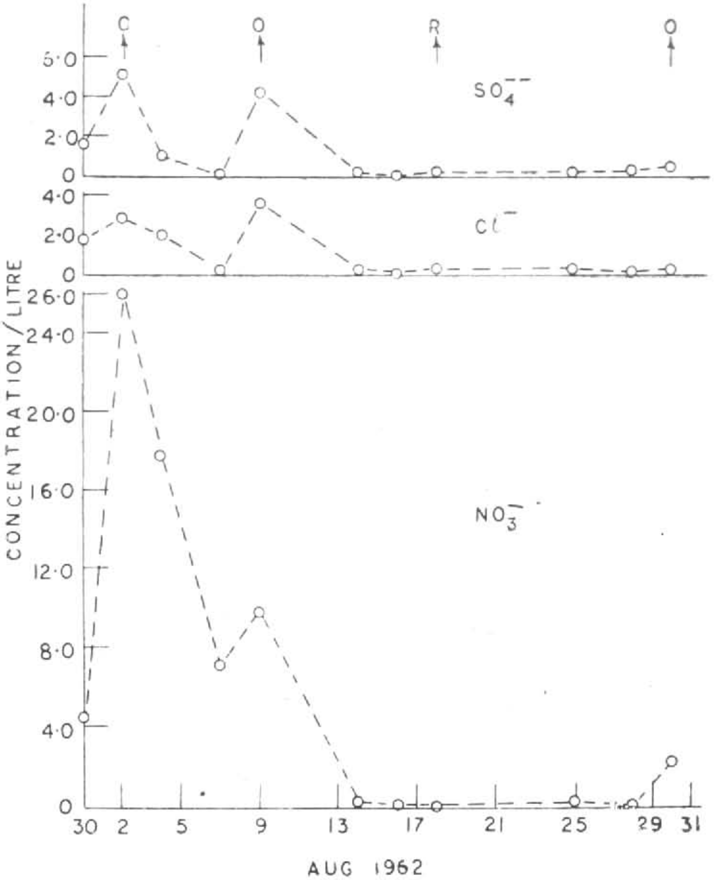

Fig. 1(c). Daily variation in concentration (number per litre) of nitrate, chloride and sulphate particles in the atmosphere at Delhi

O—Overcast, R—Rain

mostly nitrates as on 7 August 1962 and 9 January 1961 or sulphates as on 5 January 1961 and chlorides as on 5 May 1961 (not shown in the figure).

(*b*) *Association with weather*

Examination of the day-to-day concentrations of the three components studied showed, in general, marked increase in their values on overcast days not immediately preceded by rain and on days of rain preceded by dry weather—thus pointing out the possible influence of maritime air on the chemical state of the atmosphere over the place. However, measurements made on occasions preceded by either heavy downpour or continuous rain indicated a decrease in all the three components, a feature which may be attributed mainly to the effects of washing. A sharp increase in the three constituents after the passage of a duststorm (not accompanied by rain) has been generally noted during the pre-monsoon period.

(*c*) *Estimation of aerosol masses forming nitrates, chlorides and sulphates*

From measurements of size distribution of droplets at different humidities, it is possible to estimate using the equation given by Wright (1936) the masses of the atmospheric particulate matter forming

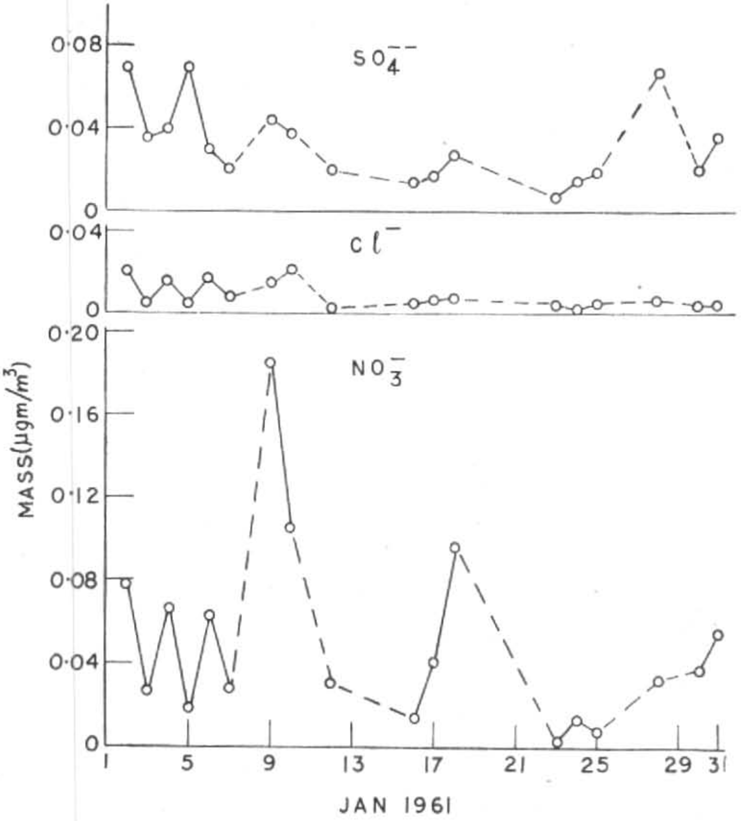

Fig. 2(a). Daily variation in concentration (mass in micrograms per cubic metre) of nitrate, chloride and sulphate particles in the atmosphere at Delhi

nitrates, chlorides and sulphates in the three different size groups A, B and C separately. From such calculations the total mass of aerosols constituting nitrates, sulphates and chlorides can be computed on any day. The daily variation in the chemical composition of aerosols as estimated in this manner for three representative months, January 1961, May 1962 and August 1962 are given in Figs. 2 (a) to 2 (c). It is to be seen from these figures that the atmosphere is relatively less polluted with hygroscopic material during the hot weather period than during either winter or monsoon. The maximum concentrations recorded of nitrates, sulphates and chlorides in the monsoon months are 16·0, 11·3 and 2·1 micrograms per cubic metre (of air). The corresponding values of the three components in winter and summer months are 0·19, 0·07, 0·02 and 0·03, 0·02, 0·02 respectively. The mean monthly values of the three components in monsoon, winter and summer periods are 3·3, 1·5, 0·4; 0·05, 0·03, 0·01; 0·01, 0·01, 0·01 micrograms/m³. The prominent weather developments over the region during monsoon and winter appear to contribute significantly to the large increases registered in the atmospheric particulate matter during those periods.

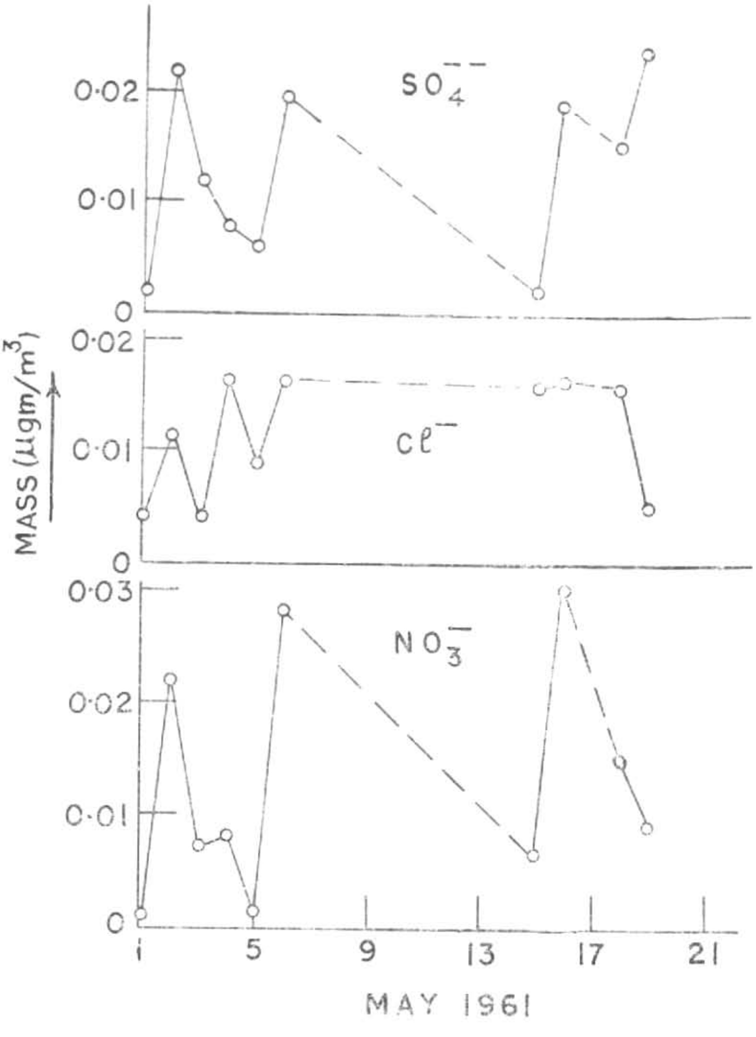

Fig. 2(b). Daily variation in concentration (mass in micrograms per cubic metre) of nitrate, chloride and sulphate particles in the atmosphere at Delhi

Measurements were available upto 19th

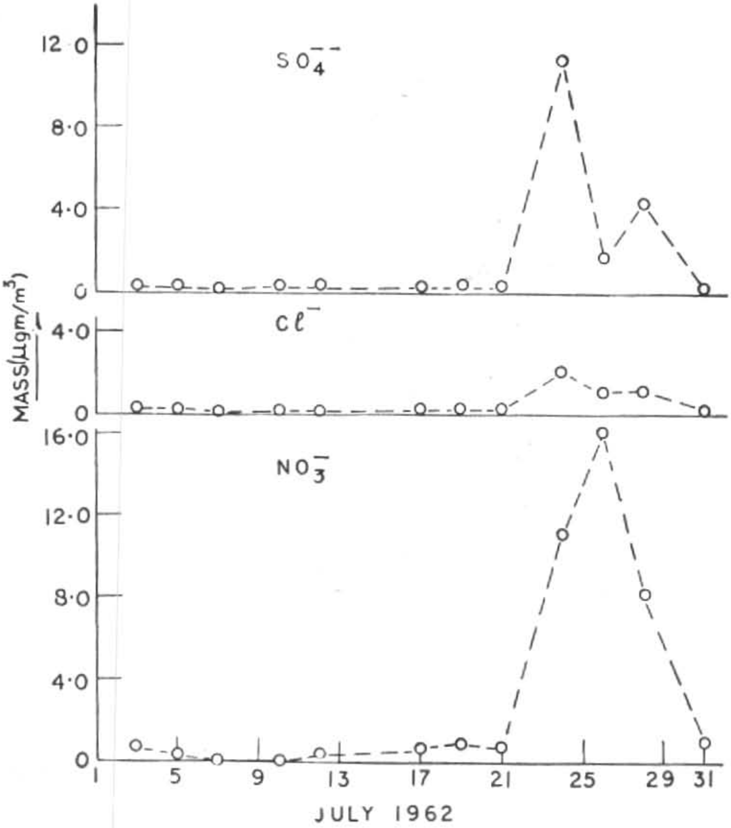

Fig. 2 (c). Daily variation in concentration (mass in micrograms per cubic metre) of nitrate, chloride and sulphate particles in the atmosphere at Delhi

4. Discussion

In classifying aerosols into three important constituents (nitrates, chlorides and sulphates), all particles showing phase transition at the fixed humidities (43,67 and 80 ~ 100 per cent) have been classified as nitrates, chlorides or sulphates. But, we can see from Table 1 that while this classification is reasonably valid for identifying chlorides and sulphates, it is not so satisfactory where the nitrates are concerned. This is because mixed nuclei consisting of $NaCl+KNO_3 + NaNO_3$ show a phase transition below a relative humidity of 43 per cent. As the presence of NaCl in the atmosphere has been established beyond doubt (Twomey 1954) it is possible that a reasonable fraction of aerosols classified under nitrates in this study may be actually chloride in nature. The fact that it is so is being further confirmed by the trend of results of the chemical analysis of rain water samples collected at Delhi.

It is suggested by the present measurements that nitrates, and other salts containing nitrates, occur in appreciable amounts in the atmosphere over Delhi. They constitute a good portion of the giant hygroscopic nuclei which are necessary for initiating the formation of rain in clouds. The marked increase in the concentration of these particles with the influx of maritime air over the area suggests that their origin is over the sea. According to Junge (1958), nitrates are possibly formed in sea salt particles in coastal areas when they come in contact with the higher concentrations of nitrates in continental air. The dependence of chloride and sulphate contents on weather, as indicated earlier, lends support to the suggestion that their origin is from the sea. The investigations of Junge (1954), however, indicate that sulphates are more of continental origin.

All the components were seen to decrease significantly in concentration between November and May. It will be interesting to compare the mass concentrations of these components with similar data obtained by Junge at Frankfurt, Florida and Round Hill by using a different technique. Measurements at Delhi have indicated that nitrates, chlorides and sulphates occur in concentrations of about one microgram/m^3 in the month of July. However, during the winter and summer periods the values at Delhi decrease by as much as two orders of magnitude. Observations by Junge at Florida and Round Hill (Junge 1956) in the months of June July also showed that Cl^-, SO_4^{--}, NO^-_3 occur in mean values of about one microgram m^3.

Measurements showing higher mean concentrations of sulphates and nitrates in winter than in summer, Figs. 2(a) to 2(c), demonstrate the influence of continental air masses on atmospheric particulate matter over the region. The travelling western disturbances which control the weather of north west India in winter months make the place rich in continental air showing features somewhat similar to those of extra-tropical latitudes. Measurements at Frankfurt by Junge (1956) have also indicated a relative abundance of SO_4 in winter as compared to summer.

Although it is seen from the measurements that the level of hygroscopic aerosol content is quite low in summer and winter months, when compared to the monsoon period, an analysis of rain samples collected over the area in different periods do not reveal significant difference in the chloride and sulphate contents. The observations, perhaps, suggest that mixing (between different layers in the atmosphere) is more complete in the monsoon season than in the rest of the year. It is also possible that the increased residence time of aerosols in winter and summer due to less frequent rain during those periods is responsible for the general level of the chemical contents of rain to remain the same whatever be their period of collection. More definite information in this direction will be only possible by direct measurements of aerosols from aircrafts extending upto cloud heights.

5. Conclusion

Twomey (1953) has made a detailed study of the phase transition technique with a more elaborate set up providing airstream of variable humidity. He found that in the case of single chemical compounds the phase change from solid to liquid always took place at sharply defined relative humidities. If, however, particles are to be examined only at a few specified humidities, as in the present study, they cannot be correctly identified. They can only be classified to a rough degree of approximation as belonging to a few different groups of substances.

The phase transition technique, has certain limitations. They are mainly—(1) the relatively small size particles undergoing transition at a particular humidity and (2) the classification of mixed nuclei becomes rather ambiguous. Nevertheless, compared to some of the more elaborate methods used for identification of aerosols of different chemical composition (Feigl 1947, Junge 1953 and Lodge 1954), the one employed here is extremely simple.

It has not been possible in course of the present study to make measurements on each and every day in the month. It is hoped that a daily systematic study over a reasonable period will enable suitable criteria to be formed for judging the history of air masses over the area, and also for finding out how any particular day is to be considered suitable or not for undertaking cloud seeding experiments.

6. Acknowledgement

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APPENDIX

The equation expressing the equilibrium condition between droplets and aqueous vapour which is used to find the radius of nuclei in equilibrium with air of given relative humidity (Wright 1936), is

$$\frac{H}{100} = \text{Exp}\left(\frac{2\,T}{\sigma R\theta r}\right) - \frac{750\,mc}{\pi r^3 \sigma\, w}$$

where, H is the relative humidity,

T the surface tension,

σ the density of the liquid,

R the gas constant for the vapour,

θ the temperature of the droplet,

r the radius of the droplet,

m the mass of the solute,

w the molecular weight of the solute,

and c a quantity which depends on the nature of the solute and for a given solute varies slightly with the concentration.

Denoting P by $2T/\sigma R\theta$ and ϕ by $750\ c/\pi\sigma w$ and expanding the exponential and neglecting the second and higher powers of P/r, the above equation becomes

$$\frac{H}{100} = 1 + \frac{P}{r} - \frac{\phi m}{r^3},$$

which has been used for calculations in the present study. The value of $1/\phi$ in respect of nitrates, chlorides and sulphates is taken as 8·8, 6·0 and 13·0 as applicable to sodium nitrate, sodium chloride and ammonium sulphate respectively.