Source of origin of ice-forming aerosols as suggested by measurements on the soluble and non-soluble components of rain water

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ABSTRACT

Samples of rain water have been collected on days of ice nuclei measurement, which have been associated concurrently with rain and categorised as high and low ice nuclei days. The soluble component in the rain water has been analysed for chloride, sulphate, sodium and calcium. The non-soluble component present has been estimated in terms of percentage reduction in transmittance of the rain water. Analysis of data has indicated that the chemical state of the air, in so far as its soluble component (hygroscopic part) is concerned, is not markedly different on the high and low ice nuclei days. The non-soluble component (non-hygroscopic part) is, however, consistently high on the high ice nuclei days. The findings point out that the natural ice nuclei are predominantly of land origin.

1. Introduction

Ice-forming nuclei play an important role in the release of precipitation from supercooled clouds by the well known Findeisen–Bergeron mechanism. As these nuclei constitute a very tiny fraction of the particulate matter in the air, investigations on their source of origin by the method of direct identification (Isono, 1955; Kumai & Francis, 1962; Byers, 1965) pose probblems and involve painstaking efforts. Also, the methods used in some of these studies have not been free from objection (Mossop, 1963). Studies made by other means have indicated that the source of origin of the natural ice-forming nuclei could be terrestrial (Price & Pales, 1964) and also extraterrestrial (Maruyama & Kitagawa, 1967). Among the terrestrial sources pointed out, there is controversy whether it is the land (Isono *et al.*, 1959) or the sea (Brier & Kline, 1959) which is the source region for the nuclei. Studies made at Delhi (Ramana Murty *et al.*, 1967) have indicated that it could be both. However, more recent investigations (Kapoor *et al.*, 1969) have suggested that the land is the dominant source region. The problem is examined further below in the light of other available data.

2. Method

In the previous studies reported (Ramana Murty *et al.*, 1967; Kapoor *et al.*, 1969) daily measurements have been made concurrently on the ice-forming and other forms of nuclei (hygroscopic and non-hygroscopic) by impaction techniques using Millipore filters and cascade impactors respectively, and inferences have been drawn on the basis that a substantial fraction of the hygroscopic nuclei measured originates from the sea while the non-hygroscopic nuclei originate from the land. In the present investigation, which is limited only to rainy days, samples of rain water have been collected on the days of ice nuclei measurement which have been concurrently associated with rain and the soluble and the non-soluble components in the rain water, which respectively reflect the hygroscopic and the non-hygroscopic nuclei state of the air, have been studied. The source of the ice-forming nuclei has been argued on the basis that (i) the non-soluble component present in the rain water is from land, (ii) certain constituents of the soluble components measured are also from land and (iii) certain other constituents of the soluble component measured are from the sea. For purposes of (ii)

and (iii) it has been considered, though subject to reservations, that bulk of chloride and sodium in rain water is from the sea and that of sulphate and calcium is from land (Junge, 1963).

3. Measurement

Samples of rain water have been collected at Poona (18°32′ N, 73°51′ E, 559 m A.M.S.L. and 110 km from the coast) on 10 days of nuclei measurement during one premonsoon and monsoon period and on six days of nuclei measurement during one period of rainfall in winter. The soluble component in the rain water has been analysed for chloride, sulphate, sodium and calcium which form its main bulk. The method followed for the collection of rain water samples and the techniques adopted for the chemical analysis are as given before (Khemani & Ramana Murty, 1968). The non-soluble component in the rain water has been estimated in terms of the percentage reduction in its transmittance. The procedure followed for this purpose has been to measure the transmittance of the rain water with Bausch & Lomb Colorimeter, at 500 millimicrons, before and after passing the rain water through a graded fritted filter. Grade no. G-5 filter (Jena^{er} Glaswerk Schott & Gen., Mainz) whose indicated maximum pore size is 1.0 to 1.7 microns has been used for filtration because of the possible reason that the ice-forming nuclei mainly lie in the size range 0.2 to 2.0 microns (Bigg, 1960; Georgii & Kleinjung, 1967). The concentration of the ice-forming nuclei has been measured by Millipore filters at −15°C (Bigg *et al.*, 1963).

The time of air sampling for the ice nuclei measurements was in the afternoon hours and the duration of sampling was generally for half-an-hour. Sampling was done from the terrace of the second floor of the office building which was reasonably free on the sides. The rain water samples were collected mostly in the evening hours when it rained during that period. The time gap between air sampling and rain water collection was usually 2–3 hours. The observational days were classified into two categories, namely, high and low ice nuclei days, depending upon whether the concentration of the ice-forming nuclei measured on the day was a few per cubic metre or a few tens per cubic metre. The data collected during the premonsoon and monsoon and during winter were presented separately as the synoptic situations governing rain development during the two periods were different.

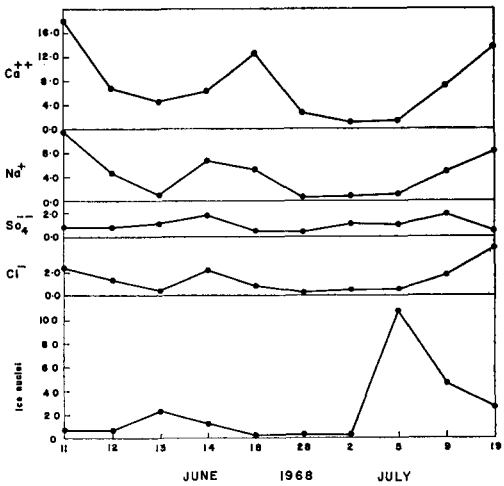

Fig. 1. Concentration of ice nuclei (no./m³ at −15°C) in the air and ionic concentrations (in ppm) in rain water.

4. Results and analysis

(a) Premonsoon and monsoon

Observations were made during June and July 1968. The period upto the middle of June was characterized by premonsoon thundershowers. The rainfall in the latter half of June and in July was of typical monsoon type, i.e. of nearly continuous type precipitation. During the monsoon season (the period June to September is termed as monsoon) strong westerlies prevail in the lower troposphere and prominent weather developments take place in the region when there is a trough of low pressure near the west coast.

(i) *Variation in the concentration of ionic components in rain water and ice nuclei in the air*

The concentrations (in ppm) of the anions and cations in the rain water and the concentration of the ice-forming nuclei (number per m³ at −15°C) in the air as measured on the rainy days are shown plotted in Fig. 1. The concentrations of chloride, sodium and also of calcium varied on nearly parallel lines, indicating a common source for these three components. The features relating to sodium and calcium as observed

Table 1. *Anion and cation concentrations and ionic ratios in rain water (premonsoon and monsoon)*

Date	Cl^-	SO_4^{--}	Na^+	Ca^{++}	$\frac{Cl^-}{Na^+}$	$\frac{SO_4^{--}}{Cl^-}$	$\frac{Ca^{++}}{Na^+}$	Ice nuclei (no./ m^3 at $-15°C$)
				High ice nuclei days				
13.6.68	0.5	1.1	1.0	4.5	0.50	2.20	4.50	23.3
14.6.68	2.2	1.8	6.7	6.3	0.33	0.82	0.94	13.3
5.7.68	0.5	1.0	1.1	1.3	0.45	2.00	1.18	106.7
9.7.68	1.8	1.8	4.8	7.1	0.38	1.00	1.48	46.7
19.7.68	4.0	0.5	8.1	13.5	0.49	0.13	1.67	26.7
Average	1.8	1.2	4.3	6.5	0.43	1.23	1.95	43.3
				Low ice nuclei days				
11.6.68	2.4	0.8	11.5	18.0	0.21	0.33	1.57	6.7
12.6.68	1.4	0.8	4.6	6.8	0.30	0.57	1.48	6.7
18.6.68	0.9	0.5	5.2	12.5	0.17	0.56	2.40	3.3
28.6.68	0.3	0.4	0.7	2.7	0.43	1.33	3.86	3.3
2.7.68	0.5	1.1	0.8	0.9	0.63	2.20	1.13	3.3
Average	1.1	0.7	4.6	8.2	0.35	1.00	2.09	4.7

during this period and also during winter (the features observed during winter are referred to later) are in contrast with those observed by Georgii & Kleinjung (1967) according to whom calcium and sodium in the total mass of the aerosols chemically analysed at the Taunus observatory on Mount Kleiner Feldberg showed anti-parallel trend. The considerable amounts of calcium which are noticeable along the coast (Junge, 1963) perhaps account for the seemingly observed parallel trend of calcium with chloride and sodium in a place like Poona which is not remote from the sea. The sharp rise in the content of ice nuclei noticed as on 13.6.68 and 5.7.68 occurred when the values of these three components measured were low or remained low at their previous values. The progressive fall in the ice nuclei content noticed towards the end of the observational period took place when there was simultaneous rise in the concentration of these ionic components. These features suggest that the ice nuclei vary either independently of or sometimes anti-parallel to the variations in the soluble component of the particulate matter in the air. The correlation coefficient (r) obtained between the ice nuclei and each of the ionic components measured is given below. The correlation coefficients are not significant at 10 per cent level.

	Cl^-	SO_4^{--}	Na^+	Ca^{++}
$r =$	−0.09	+0.25	−0.25	−0.32

If the chloride is considered, as it should be, to be largely from the sea (the place of observation is only 110 km from the coast and is directly under the maritime flow), the observations suggest that the sea is not the predominant source of origin of the ice-forming nuclei. Sulphate is not closely related with the other three ionic components (see Fig. 1) suggesting that its source of origin (sulphate is considered to be predominantly from land) is independent of the rest. Note that the correlation with sulphate, though found to be equally small as with the other ionic components, is of opposite sign, i.e. positive, suggesting land influence on the ice nuclei.

(ii) *Ionic ratios in rain water on the high and low ice nuclei days*

Departures of the ionic ratios, chloride to sodium, sulphate to chloride and calcium to sodium from the corresponding values for sea water which are respectively 1.8, 0.14 and 0.04 may be considered as useful index of the land and the sea influence on the chemical state of the air in the region (the limitation of such assumption with regard to chloride to sodium was discussed by Rossby & Egner, 1955). The concentrations of the anions and cations and the values of the ionic ratios are given datewise in Table 1 for the high and low ice nuclei days separately which numbered five each. Chloride, sodium and calcium varied within wide limits—by one order of magnitude or more as compared

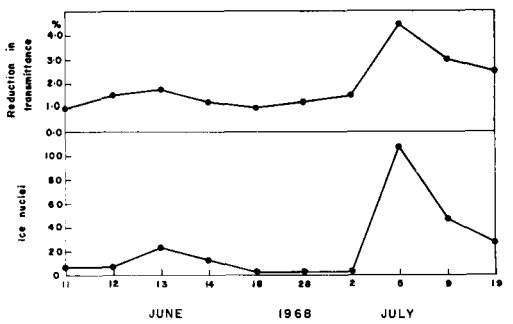

Fig. 2. Concentration of ice nuclei (no./m³ at −15°C) in the air and percentage reduction in transmittance of rain water.

to sulphate—both on the high and low ice nuclei days. The values of the ionic ratios which indicated strong continental influence, though the place of observation is only 110 km from the coast, also varied equally widely on both the categories of days. On the average, the ionic ratios are about the same irrespective of the ice nuclei content in the air. The features point out that the concentration of the ice nuclei is not closely dependent upon the chemical state of the air in so far as the soluble component considered is concerned, be it of land or sea origin.

(iii) *Concentration of non-soluble component on high and low ice nuclei days*

If there is no marked difference, as indicated above, in the constituents of the soluble component of the particulate matter in the air on the two categories of days, the question naturally arises whether there is difference in the non-soluble component on such days. For this purpose the concentrations of the suspensoids, as measured in terms of the percentage reduction in transmittance of the rain water samples collected, have been considered and these values are illustrated in Fig. 2. The observations suggest that the concentration of the non-soluble component in rain water is markedly high on the high ice nuclei days. The ice nuclei in the air showed correlation of +0.96, significant at 1 per cent level, with the non-soluble component in the rain water. Note the three-fold increase which occurred in the percentage of reduction in transmittance on 5.7.1968 as compared to 2.7.1968, when the ice nuclei content increased by more than an order of magnitude. On the average, the rain water on the high ice nuclei days showed twice as much reduction in transmittance (2.6 per cent) as it was on the low ice nuclei days (1.25 per cent).

(*b*) WINTER

Fewer observations were available during this period. These were made from 11th to 16th December, 1967 when the region experienced wet weather under the joint influence of a low pressure system which had passed from the west at higher latitudes (western disturbance) and a depression which had moved from the east at lower latitudes. The prevailing winds during winter (December to February) are from the east.

(i) *Variation in the concentration of ionic components in rain water and ice nuclei in the air*

The values of the anions and cations datewise together with the daily concentration of the ice nuclei measured are shown in Fig. 3. The values of the ionic concentrations varied much less during this period than during the monsoon. Chloride, sodium and also calcium varied in a similar manner as during the monsoon, i.e. on nearly parallel lines, indicating that these three have a common source of origin during the winter period too, when the prevailing wind direction is easterly as compared to the westerly during the monsoon. Sulphate varied the least as during the monsoon. Unlike in monsoon, the chloride showed association with the ice nuclei indicating influence of marine nature on the latter. However, as the air stream in the region has a longer land history during this period (the prevailing easterly flow during the winter

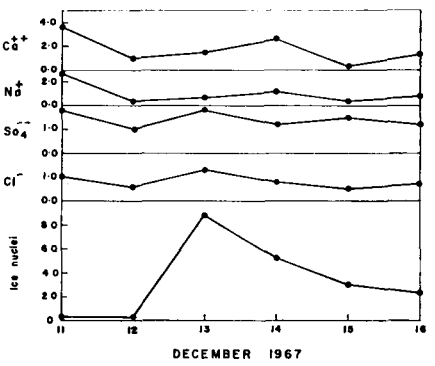

Fig. 3. Concentration of ice nuclei (no./m³ at −15°C) in the air and ionic concentrations (in ppm) in rain water.

Table 2. *Anion and cation concentations and ionic ratios in rain water (Winter)*

Date	Cl^-	SO_4^{--}	Na^+	Ca^{++}	$\frac{Cl^-}{Na^+}$	$\frac{SO_4^{--}}{Cl^-}$	$\frac{Ca^{++}}{Na^+}$	Ice nuclei (no./m^3 at $-15°C$)
				High ice nuclei days				
13.12.67	1.3	1.8	0.7	1.5	1.86	1.38	2.14	89.0
14.12.67	0.8	1.2	1.2	2.6	0.67	1.50	2.17	53.0
15.12.67	0.5	1.5	0.4	0.3	1.25	3.00	0.75	30.0
16.12.67	0.7	1.2	0.8	1.3	0.88	1.71	1.63	23.3
Average	0.8	1.4	0.8	1.4	1.17	1.90	1.67	48.8
				Low ice nuclei days				
11.12.67	1.0	1.8	2.7	3.6	0.37	1.80	1.33	3.3
12.12.67	0.6	1.0	0.4	1.0	1.50	1.67	2.50	3.3
Average	0.8	1.4	1.6	2.3	0.94	1.74	1.92	3.3

covers a much longer land path than the prevailing westerly flow during the monsoon) possibility of chloride of continental origin entering into the rain cycle is not ruled out. The other three ionic components showed no close association with the ice nuclei as during the monsoon. The following are the correlation coefficients (r) between the ice nuclei and the different ionic components measured.

	Cl^-	SO_4^{--}	Na^+	Ca^{++}
$r=$	+0.62	+0.36	−0.29	−0.11

The correlation coefficients are not significant at 10 per cent level. On the whole, there is no distinct association found between the ice nuclei and the different constituents of the soluble component in the rain water.

(ii) *Ionic ratios in rain water on the high and low ice nuclei days*

Out of the six observational days available two were associated with low ice nuclei concentration. The ionic concentrations and the ionic ratios were given in Table 2, for the high and low ice nuclei days separately.

The values of the cations and anions varied equally widely on both the categories of days, though the extent of variation noticed is not as much as it was during the monsoon. The ionic ratios also varied equally widely on both the categories of days. On the average, the ionic ratios are nearly the same on the high and low ice nuclei days. Though the number of observational days available during the period is small, the available data tend to suggest that the chemical state of the air on the one category of days is not markedly different from that on the other category as far as the soluble component studied is concerned.

(iii) *Non-soluble component in rain water*

The percentage reduction observed in the transmittance of rain water (non-soluble component) and ice nuclei content of the air measured are illustrated datewise in Fig. 4. The non-soluble component is markedly high on the high ice nuclei days. The observations showed a correlation coefficient of +0.95, significant at 1 per cent level. Note the sharp increase (more than four-fold) which was noticed on 13.12.1967 as compared to the previous day, when the ice nuclei content rose by more than an order of magnitude. On the average, the reduction noticed in the transmittance of rain water on the high ice nuclei days is 2.4 per cent as against 1.0 per cent on the low ice nuclei days.

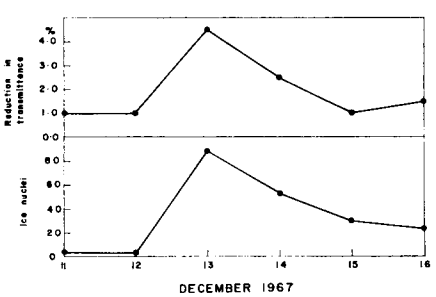

Fig. 4. Concentration of ice nuclei (no./m^3 at $-15°C$) in the air and percentage reduction in transmittance of rain water.

5. Discussion

The soluble (hygroscopic) components in rain water, except for chloride during winter (the observed parallel trend of chloride with the ice nuclei during winter does not fit the general pattern of results), are poorly correlated with the ice nuclei content in the air. See the values of the correlation coefficient which are given under 4(*a*) (i) and 4(*b*) (i) for monsoon and winter separately. But, the non-soluble (non-hygroscopic) component in the rain water and the ice nuclei content in the air are surprisingly very closely related both during the monsoon and winter. The same features are reflected when the data obtained during the two observational periods are also combined and considered together, for in that case the correlation coefficient with respect to the different soluble components, namely, chloride, sulphate, sodium and calcium, works out to be respectively -0.05, $+0.31$, -0.03 and -0.30 not significant at 10 per cent level, but that with respect to the non-soluble component works out to be $+0.94$, significant at 1 per cent level. Considering that the non-soluble component of the aerosols is mainly of land origin, the findings point out that the predominant source region of the ice-forming nuclei is the land. Measurements made recently in England (Stevenson, 1968) have revealed that a large proportion of the total number of the ice-forming nuclei in that region are of continental origin.

The observed marked contrast in the non-soluble component and the non-contrast in the soluble component on the two categories of the nuclei days considered in the present study further suggest that (i) a sizable fraction of the natural ice nuclei contains little hygroscopic matter, and (ii) the nuclei consist systematically of non-hygroscopic material. The inference which is but qualitative in nature is broadly in agreement with some of the direct measurements by Byers (1965) according to whom no hygroscopic material was identified under the electron microscope in the 36 replicas of the ice crystals formed in a sampling cold chamber at -15°C. The majority of the identifiable particles, assumed to be the ice nuclei in the replicas examined were found to be clay minerals.

Conclusion

The method of approach, as attempted, appears to be promising. The study, in suggesting that the natural ice nuclei are of land origin, pointed out that the non-soluble component in rain water could form a useful index of the ice nuclei content in the air. However, keeping in view that the concentration of the ice nuclei could vary sometimes within wide limits in course of the day and also because the nuclei concentrations referred to in the study related only to some half-an-hour period of sampling in the afternoon hours on the day of rain occurrence, it is considered that more data are needed before the generalization is valid. No attempt has been made to obtain the actual concentration and size distribution of the non-soluble particulates in the rain water and these should be known through refined techniques of measurement (Kratohvil, 1964). Also, it will be of added interest if the ice nuclei content of the rain water itself (Vali, 1968) is simultaneously investigated, for in that case it would be possible to obtain a better insight into the ice nuclei state of the air vis-a-vis the non-soluble particulates in it.

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ИСТОЧНИК ПРОИСХОЖДЕНИЯ ОБРАЗУЮЩИХ ЛЕДЯНЫЕ ЧАСТИЦЫ АЭРОЗОЛЕЙ, ПРЕДПОЛАГАЕМЫЙ ИЗМЕРЕНИЯМИ РАСТВОРИМЫХ И НЕРАСТВОРИМЫХ КОМПОНЕНТ ДОЖДЕВОЙ ВОДЫ

Были собраны пробы дождевой воды в дни измерений ядер зарождения ледяных частиц, которые были связаны с дождями и подразделены как дни высокой и низкой концентрации этих ядер. Растворимые компоненты в дождевой воде были проанализированы на хлориды, сульфаты, калий и кальций. Присутствие нерастворимых компонент было оценено по уменьшению прозрачности дождевой воды. Анализ данных показал, что химическое состояние воздуха в отношении растворимых компонент (гигроскопическая часть) не отличается заметно для дней высокой и низкой концентрации ядер. Однако содержание нерастворимых компонент (негигроскопическая часть) постоянно выше в дни высокой концентрации ядер. Это указывает, что ядра зарождения ледяных частиц преимущественно почвенного происхождения.