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Deactivation of the ice-forming aerosols by chlorine

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ABSTRACT. Tests conducted with very large amounts of chlorine-in-air (~1000 ppm) have shown that chlorine inhibits the nucleating activity of natural ice-forming nuclei in the air by a factor of only about 5 at –15°C, implying that it is no effective deactivator to be considered for possible use in weather modification studies.

1. Introduction

The nucleating efficiency of a crystalline substance depends critically upon its surface structure and, therefore, its activity may be considered to deteriorate under certain environmental conditions. Ice-forming aerosols which initiate rain in supercooled clouds, and the majority of which has been identified by Kumai and Francis (1962) and by Byers (1965) as constituting clay minerals, suffer deactivation by certain gaseous contaminants due possibly to the poisoning effects, by such contaminants, of the favourable nucleation sites on the surface of the aerosols. Schaefer (1950) reported the presence of appreciable quantities of wood and coal smoke as cause for deactivation. Georgii (1960) pointed out that increasing concentrations of of NH_3, NO_2, and SO_2 deteriorate their activity. Also, Georgii (1963) demonstrated the deactivation effects of these gases in a number of inorganic and organic ice nuclei. But, Reynolds *et. al* (1952), working on ice-crystal information on silver iodide particles, found that the presence of small amounts of ammonia accelerated the activity of silver iodide. Little work has, however, been reported on the effect of chlorine on the nucleation of ice forming aerosols. Junge (1956) has established from measurements at Florida that chlorine is present in the atmosphere in the form of giant size particles and gaseous compounds (most likely to be HCl or Cl_2) and that the gaseous component comprises about one half of the total chloride. As it has been shown by Sekhon and Ramana Murty (1965) that chloride constitutes an important component of the atmospheric aerosols even in well inland regions at Delhi, an understanding of the possible influence of gaseous chlorine compounds on the nucleating efficiency of the ice nuclei in the air is of importance. An attempt is made in the following to investigate the effect of chlorine gas on the natural ice nuclei. Only very large concentrations of chlorine (~1000 ppm) as are many orders of magnitude higher than the atmospheric gaseous Cl concentration ($\sim 10^{-3}$ ppm) have been considered in the present study.

2. Equipment and measurements

The equipment employed for the investigation is a 5-litre mixing type cloud chamber which is similar to what has been described and used earlier for the ice nuclei measurement by Prabhakar and Ramana Murty (1962). The salient features of the equipment and of the method of measurement are mentioned here. Air in the 5-litre chamber is cooled by means of liquid air, to different temperatures, in steps of 4°C, in the temperature range from —10°C to —30°C. The ice crystals formed on the natural ice forming nuclei in the sample of air cooled are allowed to grow to big enough sizes for detection in super cooled sucrose solution kept at the bottom of the chamber. The number of ice crystals formed in successive fresh samples of air taken for measurement at different temperatures in each series of the observations made has been counted, which formed the basic data. The concentrations effective at temperatures —15°,—20° and —25°C have been determined from the data thus collected. Measurements have been made, in the first instance, without adding chlorine to the air in the chamber. Later, the procedure of measurement is repeated after adding known amount of freshly prepared chlorine to the air samples taken in the chamber. The time gap between the two series of measurements made, *i.e.*, without and with chlorine, has been kept to a minimum of about an hour, where possible, in order to minimize the errors due to the possible short-period fluctuations in the content of the natural ice nuclei. The chlorine gas introduced has been prepared using standard laboratory technique. The gas-air concentration ratio arbitrarily chosen for the study has been 1 : 1400, expressed by volume. A few observations

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TABLE 1

Concentration (number per litre) of ice-forming nuclei in the air at the specified temperatures

		Temperature (°C)		
		—15	—20	—25
		1966		
Dec	17	1·0 (0·4)	8·2 (2·2)	—
	23	0·4 (0·0)	4·2 (3·2)	—
	24	9·0 (1·0)	19·4 (3·3)	14·0 (5·6)
		1967		
Apr	11	1·0 (0·2)	22·8 (2·6)	52·0 (28·0)
	14	0·4 (0·8)	5·6 (2·2)	—
	15	0·0 (0·0)	0·2 (1·2)	8·8 (5·4)
	25	0·0 (0·0)	0·6 (0·2)	—
	28	2·2 (0·6)	3·2 (1·1)	11·0 (3·0)
May	5	1·2 (0·0)	8·0 (4·5)	26·5 (11·5)
	19	0·3 (0·1)	0·8 (0·6)	—
	26	0·0 (0·0)	0·2 (0·2)	4·0 (2·2)
Jun	2	0·9 (0·0)	4·2 (1·2)	16·0 (10·8)

Values within brackets represent concentration when the ratio of chlorine to air in the chamber was 1 : 1400

have also been made at a slightly lower (1 : 2800) and a slightly higher (1 : 700) value of the gas concentration in order to confirm the observed effect.

3. Results and discussion

The concentration of ice crystals as determined in the case of air samples, without chlorine, for the three specific temperatures mentioned, *viz.*, —15°, —20° and —25°C on the 12 occasions of the experiment are given in Table 1. As the measurements made have not always extended to low enough temperatures, there are gaps in the indicated concentration under the column corresponding to —25°C. The values stated in brackets represent the concentration of ice crystals obtained on the corresponding occasions when chlorine to air ratio in the chamber was 1 : 1400.

The data in Table 1 point out that the natural ice forming nuclei suffered deactivation in the presence of chlorine, in the majority of the instances studied, at the three temperatures considered. The extent of deactivation noticed varied widely in the individual cases, slight activation also having been noticed sometimes, possibly due to uncertainties involved in the method adopted for the measurement of ice nuclei concentration in the air. On the average, as a result of adding chlorine to the air, the count of the effective ice nuclei has decreased by a factor (this factor represents the average deactivation and is given by dividing the total number of counts obtained on all the occasions experimented without chlorine by the total number of counts on all those occasions with chlorine) of 5·3, 3·5 and 2·0 at temperatures —15°, —20° and —25°C respectively (*see* figures under Col. **3** of Table 3).

The results obtained at a lower (1 : 2800) and a higher (1 : 700) chlorine to air concentration (the observations made are few and do not extend to —25°C) are given in Table 2. The data which showed a less count with chlorine than without it, on all the occasions when the experiment was conducted, confirm the deactivation effect of chlorine on the ice-forming nuclei noticed at the chlorine to air concentration ratio of 1 : 1400.

The value representing the average deactivation as found in the case of three concentrations studied are given in Table 3. The results suggest a slight increasing tendency in deactivation with concentration (the deactivation increases by more than 50 per cent with 4-fold increase in chlorine content), and also a slightly higher degree of deactivation at warmer temperatures (the deactivation is higher by about 30 per cent at —15°C than at —20°C). The features, if confirmed by further observations, may be explained as follows. If it is considered that the active spots (such as the dislocation steps), where nucleation commences on the surfaces of the natural ice nuclei, get more completely affected at higher gas concentrations, the deactivation noticed will be more, as indicated, at higher chlorine concentrations. Also, if the nuclei which are activated at warmer temperatures are larger in size—nuclei of a given substance which are activated at warmer temperature are likely to be larger in size according to Fletcher (1959), and the gross composition of aerosols on any one occasion may not have varied significantly, at least during the period of the experiment—these may possess on their surfaces more number of active spots, thereby becoming more vulnerable for deactivation.

A comparison of the results obtained with chlorine in the present study with those of Georgii (1960) in the case of ammonia shows that both these gases deactivate the natural ice nuclei nearly to the same extent. The concentration of the ice-forming aerosols active above −21°C has been reduced to 35 per cent of the normal value when the air samples tested contained 1500 ppm of ammonia.

4. Deactivation of ice-forming aerosols and liability of rain from clouds

It is possible to consider not only preactivation as reviewed by Papee (1962) but deactivation as well of the natural ice-forming nuclei. While preactivation will extend the temperature range of ice-formation on the nuclei to higher values (this might help facilitate rain-formation), deactivation by surface poisoning affects the thresholds temperature to lower values (this might help inhibit rain-formation). The suggested reduction, in the presence of chlorine, of the effective ice nuclei concentration in the air at −15°C by a factor of 5 is equivalent to reducing the threshold temperature of the nuclei by only 2·5°C according to Fletcher (1962).

Of the three gases studied by Georgii (1963), *viz.*, NH_3, NO_2 and SO_2, ammonia exhibited maximum degree of deactivation. A comparison of the results obtained in the case of chlorine as in the present study with those obtained by Georgii in the case of ammonia, as already pointed out, indicated that chlorine is not a better deactivator than ammonia. As the concentration of the ice-forming nuclei in the air is known to fluctuate by a factor of 5 or more even in the natural course, any of these inorganic trace gases appears to be of no avail to bring about deactivation in the nuclei to an extent which could be considered to be of meteorological importance. However, the possible significance of maintaining the ice nuclei in the air at reduced levels of concentration during the development and active periods of storms may have to be explored. In this connection, it is of interest to note that there are certain organic chemicals like methyl amine which could inhibit ice nucleation down to a temperature of −52°C as observed by Bristein (1957).

5. Conclusions

The study has demonstrated that chlorine inhibits the nucleating efficiency of the natural ice-forming nuclei in the air. The tests have been conducted only with very large concentrations of chlorine and these have shown that the effective ice nuclei concentration at −15°C could be reduced by a factor of about 5 when the concentration of chlorine considered was higher by 6 or more orders of magnitude than the gaseous Cl concentration generally found in the atmosphere.

Wide fluctuations have been sometimes noticed in the deactivation as found from one occasion to another. The feature is partly attributable to the equipment used in the study not having been as sensitive and reliable as is desired for

TABLE 2

Concentration (number per litre) of ice-forming nuclei in the air at the specified temperatures

	Temperatures (°C)	
	−15°	−20°
Ratio of Chlorine to air in the chamber 1 : 2800		
Apr 19, 1968	14·5 (3·2)	76·0 (49·0)
Apr 27, 1968	7·0 (3·0)	45·5 (8·5)
May 3, 1968	3·0 (1·0)	19·0 (5·5)
May 18, 1968	3·0 (0·8)	33·0 (3·0)
Ratio of Chlorine to air in the chamber 1 : 700		
Apr 26, 1968	8·0 (2·0)	36·5 (4·5)
May 4, 1968	0·8 (0·2)	5·7 (3·7)
May 17, 1968	10·0 (1·0)	38·5 (9·0)

Values within brackets represent concentration

TABLE 3

Average deactivation at the specified values of chlorine to air ratio in the chamber

Temp. (°C)	1 : 2,800	1 : 1,400	1: 700
−15	3·4	5·3	5·9
−20	2·6	3·5	4·7
−25	—	2·0	—

the purpose. The inherent pitfalls of the various types of equipment in use for atmospheric ice nuclei measurement, including those of the mixing type cloud chamber, have been mentioned by many, and more recently by Mason (1968). The results reported may, therefore, furnish only a rough estimate of the effect of chlorine as a surface poison.

Particulate pollutants also deactivate ice-forming aerosols by physically covering the nucleation sites present on the surface of the aerosols, as shown by Mossop and Thorndike (1966). Both the gaseous and particulate industrial pollutants which will be in abundance in the urban air should, therefore, affect the ice nuclei state of the air in the region and the extent to which such pollutants become responsible for the observed rainfall patterns in and around is a matter for investigation.

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