# AN ANALYSIS OF THE FILTER DIFFUSION CHAMBER AND DROP FREEZING METHODS OF DETERMINING ICE NUCLEUS CONCENTRATIONS*

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ABSTRACT

The membrane filters used for sampling at a height of 60 m and at ground level were processed with a drop freezing technique and a static vapor-diffusion chamber. Comparisons of IN concentrations obtained by the two techniques are made. The blank filter counts and ice nucleus measurement reproducibility are analysed. The factors affecting IN concentration measurements are discussed and some favorable operation conditions are suggested. It has been found that: (a) the IN concentrations typically range from 0.2 $L^{-1}$ to 2.0 $L^{-1}$ at $-20°C$, (b) significant time variations in IN concentrations occurs, (c) the IN concentrations obtained by the drop freezing technique typically exceed the value given by the diffusion chamber, (d) their variation trends are generally in phase, (e) high IN concentrations are often associated with precipitation events.

## I. INTRODUCTION

Among various techniques for measuring IN concentrations, the membrane filtration method is distinguished by several advantages. In general, the sample volume can vary from tens to hundreds of liters. The IN contained in a large volume of air can be easily collected on a very thin filter for subsequent processing in a thermal-gradient diffusion chamber with variable heights. In the chamber the temperature and humidity can be independently controlled and the himidity can be controlled with a higher accuracy than several other methods. A number of experiments have shown clearly that the IN concentration counts are critically dependent on the supersaturation in the chamber. Besides, it is unnecessary to process the filters on the spot. The results indicated that there is no difference in IN concentrations measured immediately or in the laboratory some time later; this is very important, especially for airborne IN measurements.

As for the disadvantages of IN concentration measurements with diffusion chambers, Bigg, et al.[1] pointed out that IN concentrations decrease with increasing sample volume. The well-known "volume effect" was examined by a number of investigators: Mossop et al.[2], Stevenson[3], Gagin and Aroyo[4], Lala and Jiusto[5], Huffman and Vali[6]. It can be explained as follows: a great number of hygroscopic particles are collected on the filter together with IN, with the condensation on these particles and growth of ice crystal during processing in the chamber becoming strong vapor sinks. Hence, the relative humidity in the chamber decreases and ice nuclei which lack an adequate vapor supply fail to activate.

Another disadvantage is that the diffusion chamber provides information primarily on

* The acronym IN is used for Ice Nucleus hereinafter.

deposition ice nuclei, but it is important to know IN concentration induced by other nucleation modes. It seems possible to improve IN concentration measurements with filters. Initially Schnell[7] and then Cooper[8] suggested a new technique for measuring atmospheric IN. Schnell indicated that the drop freezing technique can be used to process membrane filters so that a broad activation temperature range is covered. One purpose of this research was to compare the two different techniques used for processing membrane filters. Other objectives included the determination of: (a) any difference in IN concentrations between summertime and wintertime; (b) variation in IN concentration with precipitation processes; (c) the effect of automobile exhaust on the IN concentrations.

## II. EXPERIMENTAL METHOD

The drop freezing method adopted after numerous tests represents a combination of the features advanced by Schnell & Cooper. Sartorius hydrophobic filters with pore sizes of 0.45 micrometer were used to capture IN in one hundred liters of air. In order to insure good thermal contact and reduce background counts, the plate of the thermal-electric cooler had been covered with a thin layer of microscopic immersion oil before the sampling filter was put on the cooler. Distilled water drops were placed on the filter with a pipette, i. e., 24 drops with a 3-mm diameter on the filters. The plate was cooled at a rate of about 1°C $min^{-1}$. The plate and filter temperatures were measured with thermocouples. The IN concentration-temperature spectrum was obtained by a modified formula of Vali[9]:

$$N=\frac{f}{V(a/A)},$$

where $N$ is the IN concentration at a given temperature, $f$ is the fraction of frozen drops, $V$ is the air sample volume, $A$ is the total area of a filter, and $a$ is the area covered by each drop. One filter was processed at a time.

The filter method with the static vapor-diffusion chamber employed has been described by Lala[10], Jiusto et al.[11], and Zamurs et al.[12] In short, Sartorius hydrophobic filters with 0.45 micrometer pore-size were exposed to 100 liters of ambient air at a flow rate of 5 L $min^{-1}$. Petroleum jelly was used to seal the bottom pores of the filters prior to processing. Three exposed and one blank filters could be processed simultaneously in a diffusion chamber with 0.5 cm separation between the filters and upper (warmer) ice plate. Experiments were run at computed saturation condition (nominal RH=100 %) and at a temperature of −20°C. After 60 min the developed crystals could be observed from above with a long focal length microscope and vertical illumination.

From December 1980 to July 1981 filters were exposed twice a week on the top of a building 60 m high and at ground level near a busy highway.

## III. EXPERIMENTAL RESULTS

### 1. *Blank Filter Counts*

The 22 blank filter counts at temperature −20°C obtained with the drop freezing technique are given in Table 1. As indicated, the average IN concentration obtained by blank filters with the drop freezing technique is 0.13 $L^{-1}$, with the standard deviation being 0.078.

The number of crystals forming on blank filters in the diffusion chamber at $T=-20$°C

Table 1 · Blank Filter Counts Obtained with the Drop Freezing Technique ($T=-20°C$)

| B.F.Counts ($L^{-1}$) | 0.05–0.06 | 0.07–0.08 | 0.09–0.10 | 0.11–0.12 | 0.13–0.14 |
|---|---|---|---|---|---|
| Frequency | 1 | 9 | 1 | 2 | 1 |
| B.F.Counts ($L^{-1}$) | 0.15–0.16 | 0.17–0.18 | 0.19–0.20 | 0.21–0.22 | 0.23–0.24 |
| Frequency | 4 | 0 | 1 | 0 | 0 |
| B. F. Counts ($L^{-1}$) | 0.25–0.26 | 0.27–0.28 | 0.29–0.30 | 0.31–0.32 | 0.33–0.34 |
| Frequency | 1 | 0 | 0 | 1 | 1 |

and RH=100% can be seen in Table 2. These tabulated data yielded an average IN concentration 0.39 $L^{-1}$ with a standard deviation 0.359. The average ratio of IN concentrations obtained from blank filters to those from exposed filters in a diffusion chamber was 0.59, and its standard deviations was 0.38. The high blank filter counts obtained in a diffusion chamber was explained by Jiusto et al.[11] and Zamurs et al.[12] as follows. A blank filter that is free of condensation nuclei will attain a higher relative humidity and allow activation of IN that otherwise would not occur when processing exposed filters in a diffusion chamber.

Table 2 Blank Filter Counts Obtained with the Diffusion Chamber ($T=-20°C$)

| B. F. Counts ($L^{-1}$) | 0—0.10 | 0.11—0.20 | 0.21—0.30 | 0.31—0.40 | 0.41—0.50 |
|---|---|---|---|---|---|
| Frequency | 7 | 12 | 13 | 9 | 3 |
| B. F. Counts ($L^{-1}$) | 0.51—0.60 | 0.61—0.70 | 0.71—0.80 | 0.81—0.90 | 0.91—1.00 |
| Frequency | 2 | 3 | 2 | 1 | 0 |
| B. F. Counts ($L^{-1}$) | 1.01—1.10 | 1.11—1.20 | 1.21—1.30 | 1.31—1.40 | 1.41—1.50 |
| Frequency | 2 | 0 | 1 | 0 | 0 |
| B. F. Counts ($L^{-1}$) | 1.51—1.60 | 1.61—1.70 | 1.71—1.80 | | |
| Frequency | 0 | 1 | 1 | | |

2. *Reproducibility*

Simultaneously exposed filters (pairs typically) were processed sequentially by drop freezing and gave quite similar counts. The percentage deviation of a single filter from the set average was given in Table 3. The average percentage deviation obtained from 63 filters was 8.4 %. By contrast, Zamurs et al.[12] showed that of 888 filters processed in diffusion chamber the average percentage deviation of a single filter from the set of four was 21.7%. In order to obtain less average deviation, the horizontal temperature distribution in the diffusion chamber must be carefully controlled and periodically calibrated. On this point the drop freezing method appears more forgiving.

**Table 3** Reproducibility of the Drop Freezing Technique ($T=-20°C$)

| Reproducibility(%) | 1—2 | 3—4 | 5—6 | 7—8 | 9—10 | 11—12 | 13—14 | 15—16 | 17—18 | 19—20 |
|---|---|---|---|---|---|---|---|---|---|---|
| Frequency | 5 | 4 | 3 | 3 | 1 | 2 | 1 | 2 | 3 | 1 |

### 3. *Delayed Processing of Filters——Drop Freezing Technique*

Experiments showed that the filters used for sampling simultaneously and processed by the drop freezing technique immediately or within 1—2 weeks after collection may give some variation in concentrations, but it is unlikely to exceed the measurement error. On the other hand, it was found that IN concentration could be severely underestimated when the delay exceeded 1—2 months. In general, the filters processed within 1 to 2 months after collection gave lower concentrations than those determined with the diffusion chamber

**Table 4** Delayed Processing (Filters Sampling at 60 m Height)

| Date of Sampling | Date of Processing | Time Delay (days) | Measured Concentration by DF ($L^{-1}$) | Ratio |
|---|---|---|---|---|
| 12/23/80 | 2/10/81 | 50 | 0.15 | 0.11 |
| 1/6/81 | 3/10/81 | 63 | 0.44 | 0.15 |
| 1/8/81 | 3/10/81 | 61 | 0.45 | 0.43 |
| 1/13/81 | 3/10/81 | 56 | 0.34 | 0.94 |
| 1/15/81 | 3/10/81 | 54 | 0.54 | 0.68 |
| 1/20/81 | 3/3/81 | 42 | 0.33 | 0.51 |
| 1/22/81 | 3/10/81 | 47 | 0.39 | 0.81 |
| 1/27/81 | 3/3/81 | 35 | 0.37 | 0.71 |
| 1/29/81 | 3/5/81 | 35 | 0.25 | 0.64 |
| 2/3/81 | 3/5/81 | 30 | 0.20 | 0.80 |
| | | | | Average=0.39 |
| | | | | Standard deviation =0.23 |

**Table 5** Delayed Processing (Filters Sampling at the Ground)

| Date of Sampling | Date of Processing | Time Delay (days) | Measured Concentration by DF ($L^{-1}$) | Ratio |
|---|---|---|---|---|
| 12/23/80 | 2/12/81 | 50 | 0.31 | 0.31 |
| 1/6/81 | 2/24/81 | 49 | 0.31 | 0.14 |
| 1/8/81 | 2/24/81 | 47 | 0.16 | 0.19 |
| 1/13/81 | 2/24/81 | 42 | 0.16 | 0.23 |
| 1/15/81 | 3/10/81 | 54 | 0.33 | 0.85 |
| 1/22/81 | 3/10/81 | 47 | 0.37 | 0.69 |
| 1/27/81 | 3/3/81 | 35 | 0.20 | 0.34 |
| 1/29/81 | 3/5/81 | 35 | 0.16 | 0.39 |
| 2/3/81 | 3/5/81 | 30 | 0.22 | 0.39 |
| | | | | Average=0.39 |
| | | | | Standard deviation=0.23 |

at the time of sampling (Tables 4, 5). As Schnell[7] and Cooper[8] also observed, there are some characteristics of the nuclei and processing methods that result in IN deactivation with time. The diffusion chamber method, however, does not appear subject to this time effect, according to certain past investigations (Bigg et al.[1]).

4. *Differences in IN Concentrations obtained at Two Sites——Diffusion Chamber (DC) Processing*

In 36 of 47 cases the IN concentrations (DC) obtained at the ground sampling site were higher than those at the 60 m sampling site. Ironically, it was found that this result was different when the filters were analyzed by the drop freezing technique, of 46 cases only in 20 cases did the ground sampling site provide higher IN concentrations. Also, the average relative values were somewhat, though perhaps not significantly, different——46 vs 31 %, (Table 6 for DC, Table 7 for DF).

**Table 6** The Relative Value of IN Concentrations at Two Sampling Sites Obtained by Diffusion Chamber

| R. V. (%) | 0—10 | 11—20 | 21—30 | 31—40 | 41—50 | 51—60 | 61—70 |
|---|---|---|---|---|---|---|---|
| Frequency | 7 | 15 | 6 | 2 | 3 | 0 | 4 |
| R. V. (%) | 71—80 | 81—90 | 91—100 | 101—110 | 111—120 | 121—130 | 131—140 |
| Frequency | 0 | 0 | 2 | 2 | 1 | 2 | 0 |
| R. V. (%) | 141—150 | 151—160 | 161—170 | 171—180 | 181—190 | 191—200 | 201—210 |
| Frequency | 1 | 0 | 0 | 0 | 0 | 0 | 1 |
| R. V. (%) | 211—220 | 221—230 | 231—240 | | | | |
| Frequency | 0 | 0 | 1 | | | | |

**Table 7** The Relative Value of the IN Concentrations at Two Sampling Sites Obtained by Drop Freezing Technique

| R. V. (%) | 1—10 | 11—20 | 21—30 | 31—40 | 41—50 | 51—60 |
|---|---|---|---|---|---|---|
| Frequency | 10 | 9 | 8 | 3 | 7 | 3 |
| R. V. (%) | 61—70 | 71—80 | 81—90 | 91—100 | 101—110 | |
| Frequency | 2 | 1 | 0 | 0 | 3 | |

5. *The Ratio of the IN Concentrations Obtained by the Two Techniques* ($T=-20°C$)

Table 8 shows the ratio of the IN concentrations at 60 m obtained by the drop freezing technique (DF) to those obtained with the diffusion chamber. The average ratio is 1.70. Of 46 cases only in 9 cases are the measured IN concentrations with the standard DC higher than that with the DF method.

Table 9 is similar to Table 8, except that it pertains to the ground sampling site. The average ratio is 1.40. Similarly, of 35 cases only in 7 cases the DC yields higher IN concen-

trations. The difference in the IN concentrations obtained by the two techniques is not too great at −20°C; the reason for these differences is not clear now, though it may be caused by different modes of nucleation as suggested earlier or by inherent technique biases.

**Table 8** The Ratio of the IN Concentrations Obtained by the Two Techniques (at 60 m Height)

| Ratio | 0.5—1.0 | 1.1—1.5 | 1.6—2.0 | 2.1—2.5 | 2.6—3.0 | 3.1—3.5 |
|---|---|---|---|---|---|---|
| Frequency | 12 | 15 | 5 | 7 | 3 | 3 |
| Ratio | 3.6—4.0 | 4.1—4.5 | 4.6—5.0 | 5.1—5.5 | | |
| Frequency | 0 | 0 | 0 | 1 | | |

**Table 9** The Ratio of the IN Concentrations Obtained by the Two Techniques (at Ground Level)

| Ratio | 0.5—1.0 | 1.1—1.5 | 1.6—2.0 | 2.1—2.5 | 2.6—3.0 | 3.1—3.5 |
|---|---|---|---|---|---|---|
| Frequency | 10 | 15 | 6 | 3 | 0 | 0 |
| Ratio | 3.6—4.0 | 4.1—4.5 | | | | |
| Frequency | 0 | 1 | | | | |

6. *Time Variation in IN Concentration (at 60 m Height)*

In Fig. 1 the "daily" variation in the IN concentrations obtained by the two techniques is given.(From 20 March to 5 April measurements of IN concentration had to be stopped temporarily.) It is immediately evident that:

(1) The IN concentrations typically range from 0.2 $L^{-1}$ to 2.0 $L^{-1}$ at −20°C.
(2) Significant time variations occur.
(3) The IN concentrations by DF typically exceed the DC values.
(4) The two curve trends are generally in phase.
(5) High IN concentrations are often associated with precipitation events, no matter which technique is used.

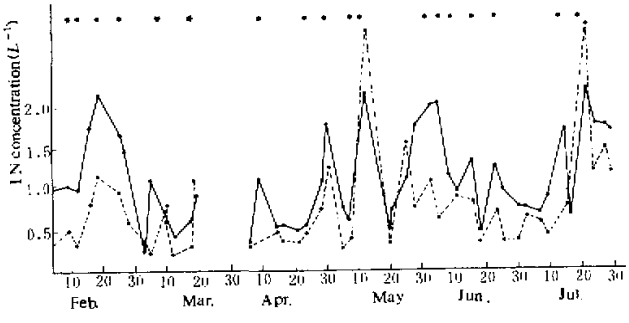


Fig. 1. Time variation of the IN concentrations obtained at 60 m by the two techniques ($T$ = −20°C).
--- DC; —— DF.

## IV. DISCUSSION

### 1. *The Effect induced by Contamination of Filter*

As indicated by experiments, filters contaminated before sampling cannot be used to measure the IN concentrations. There appeared completely irregular fibers on the contaminated filter in the diffusion chamber instead of the hexangular crystals. Sometimes only fibers appeared on the filter, sometimes both fibers and crystals were formed. If a contaminated filter was processed with the drop freezing technique, the drops were frozen at temperatures much warmer than those obtained from normal filters. Based on these measurements, it is likely that a hasty conclusion would be drawn that a very high concentrations of IN existed in the atmosphere. In fact, even a blank filter, if it was contaminated before sampling, gave very high value of IN concentrations.

Preliminary analysis of contaminated blank filters with Scanning Electron Microscope and Energy Dispersive X-Ray Microanalyzer showed that the filter was composed of similar chemical elements to the normal one, but the ratio between chemical elements for contaminated and normal filters seemed somewhat different. For normal filter, for example, the ratio of silicon to phosphorous, sulphur and titanium in weight were 0.157, 0.072 and 0.140 respectively, for contaminated one they were 0.006, 0.001 and 0.007 respectively. The effect of contamination on the ice nucleation behavior is worth studying in more detail.

It is important to know the background concentration of blank filter for measuring IN concentrations, especially when high IN concentrations are measured. If remarkably higher background concentrations than those given in this paper are obtained, the contamination of the filter may be considered as one of the possible explanations.

### 2. *The Effect of Frost——Drop Freezing Method*

As the plate temperature is decreased, the drops are frozen one by one, in the meantime on the filter some frost occurs near and around the frozen drops. It is likely that some drops would be frozen by lateral frost propagation rather than by ice nucleation. Hence the measured IN concentration would be overestimated. For example, the two simultaneously sampling filters working on 18 June were processed by the DF method. One filter count was 0.44 $L^{-1}$ (at temperature $-20°C$), but the other one even approached 1.74 $L^{-1}$ due to the effect of frost.

It is impossible to avoid frost on the filter when drops begin to freeze. But in order to reduce its effect, processing must be made in an environment with reasonably low humidity. Moreover, it is critically important to choose a suitable number (not too high) and size of drops on the filter, as closely packed drops can interact once freezing begins. As a drop freezes, the latent heat of fusion causes its temperature to approach 0°C. A tremendous vapor pressure gradient and supersaturation is created around the frozen drop, causing adjacent condensation-freezing and sheet frost propagation. As described in the next section, microscope immersion oil tends to minimize but not completely eliminate this effect. On the other hand, with too few drops the measurement accuracy and IN concentration range would be reduced. It was determined that 24 drops with a 3 mm diameter on a filter with a 42 mm effective diameter were a good compromise.

### 3. *The Effect of the Filter Sealant——DF Method*

Most investigators believe that some kind of sealant is necessary between the plate and

filter (either filter technique). But the question arises about "which one is better?". There is no general agreement so far among investigators. Comparative studies were made in using silicon oil, paraffin oil, immersion oil (Cargille) and varnish. Finally, immersion oil suggested by Cooper[5] was used in the study primarily because it produced minimal frosting.

The question naturally arises concerning whether there is any possibility that ice nuclei would be deactivated (or covered) by the immersion oil. In an attempt to answer this question, some tests were made as follows. On half of a filter 12 drops were placed, then moved onto the cold plate already covered with immersion oil (in short, we call this the "non-standard procedure"). Alternately, the other half of each filter was first put on the plate covered with immersion oil, after the oil penetrated the filter, another 12 drops were placed on it ("standard procedure"). The temperature at which an IN concentration of 1 $L^{-1}$ was obtained in each case is given in Table 10.

**Table 10** The Temperatures (at 1 $L^{-1}$ IN Concentration) obtained by Different Procedures

| Date | 12/31 | 1/2 | 1/6 | 1/8 | 1/13 | 2/17 | | 2/19 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Standard | −22.2 | −23.5 | −23.8 | −22.8 | −24.0 | −19.7 | −18.6 | −14.2 | −14.4 | −14.0 | −15.0 |
| Non-standard | −21.5 | −23.7 | −24.0 | −22.7 | −23.8 | −19.1 | −17.5 | −15.2 | −15.8 | −15.5 | −15.4 |

As indicated in Table 10, the temperatures obtained by the standard procedure were not always colder than that by the non-standard procedure which one might expect if oil was deactivating ice nuclei. Of 11 cases the maximum difference amounted to 1.5°C, the average deviation only 0.7°C. Based on the almost negligible difference and relative ease of filter preparation, it was concluded that the standard procedure of applying immersion oil be adopted for this and future studies. This does not completely solve the question of nuclei deactivation by the liquid sealant, but it suggests that the problem may not be serious.

4. *Reprocessing the Same Filter——D F Method*

After a filter was processed, the plate temperature was increased until all frozen drops were melted. Then the plate temperature was decreased again for refreezing the same drops. The same filter was reprocessed three or four times. The results are shown in Table 11, in which two filters were exposed to aerosol at 60 m and at the ground on 12 March. Table 11 shows that the more times the filter is reprocessed, the higher is the IN concentration obtained. It is worth studying further.

**Table 11** Reprocessing the Same Filter

| Sampling Site | IN Concentration ($L^{-1}$) | | | |
|---|---|---|---|---|
| | No. 1 | No. 2 | No. 3 | No. 4 |
| At 60 m | 0.43 | 0.53 | 0.55 | 0.65 |
| At the Ground | 0.61 | 0.65 | 0.76 | |

It is interesting to note that the drop freezing order was almost stable and repeatable, i. e., that the drops in contact with IN freeze in the same time (temperature) sequence on

successive filter processings. In Fig. 2 the circules represent the drop location on the filter, while the numbers to their right indicate the drop freezing order. It seems that the sequence of drop freezing is quite consistent for repeated processings and for both sampling levels.

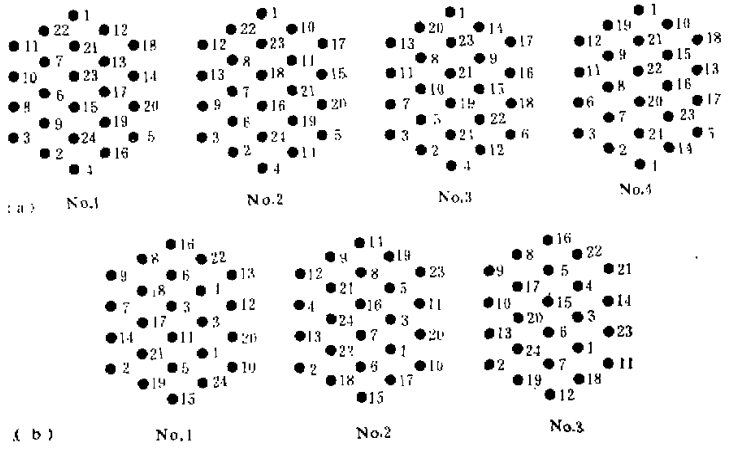


Fig. 2. The drop freezing order, (a) at height 60 m and (b) at the ground. Circles represent drop location. Numbers on their right side represent drop freezing order.

## V. CONCLUSIONS

The procedure of processing a membrane filter with a drop freezing technique may be considered as a development of the filter method for measuring IN concentration. Preliminary results showed that this kind of filter method is capable of giving lower blank filter counts, acceptable reproducibility, and seemingly reasonable values of IN concentration, at least at low temperature of $-20°C$ where most comparison tests were made. A number of factors must be carefully considered, namely: frost on the filter, filter sealant, filter contamination, delayed processing of a filter, optimum drop size, drop number and sample air volume. Without due consideration of these variables, spurious results can easily be obtained. The immersion oil sealant was the best tested.

Comparisons made for seven months show that, in general, the drop freezing technique yielded somewhat higher filter counts than that of the diffusion chamber, but this comparison was made only for 100 liter sample volumes and at a temperature of $-20°C$. At temperatures higher than $-15°C$, the drop freezing method offers far more sensitivity to detecting IN than the diffusion chamber method. How valid some of these concentrations at somewhat high temperatures will be remain to be determined.

Also, it is evident that:

(1) the IN concentrations typically range from 0.2 $L^{-1}$ to 2 $L^{-1}$ at $-20°C$;
(2) significant time variations in IN concentration occur;
(3) the daily IN variation trends obtained by the two techniques are generally in phase;
(4) high IN concentrations are often associated with precipitation events.

From the data reported in this paper, it is not possible to discern with certainty that:

(1) any significant differences in IN concentration can be found between late winter and early summer;

(2) low level aerosol containing a considerable amount of automobile exhaust constitutes an important source of IN.

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