## NOTES AND CORRESPONDENCE

# Ice Nucleus Measurements in an Urban Atmosphere[1]

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ABSTRACT

On the basis of Millipore filter measurements it is concluded that natural ice nuclei were deactivated in passing over St. Louis, Mo., during March 1973. This conclusion is supported by very strong statistical evidence.

To overcome the effects of soluble materials in desensitizing the filter technique, samples were limited to volumes less than 100 liters with the background crystal count measured for every filter; a forced-flow developing chamber was used; and the Huffman-Vali correction factor, based upon concurrently measured CCN, was applied.

The measurements strongly suggest the possibility of local sources of ice nuclei. However, these nuclei also were deactivated in passing over the city.

Simultaneous measurements with an expansion chamber gave results similar to those of the filters, but did not show statistical support.

## 1. Introduction

As part of Project METROMEX The University of Chicago Cloud Physics Laboratory is studying the extent to which an urban-industrial complex modifies cloud active nuclei and the effect of such nuclei in altering the structure and development of clouds that ingest the urban air. This paper discusses results of a series of 10 sampling flights for studying ice nuclei over and around St. Louis, Mo., during March 1973. Two techniques have been used for measuring ice nuclei—membrane filters and a Bigg-Warner expansion chamber. Most emphasis has been placed upon sampling with membrane filters because of their simplicity for field and airborne use and their adaptability for subsequent laboratory processing in a chamber where temperature and humidity can be carefully controlled.

## 2. Sampling procedures and instrumentation

Samples were collected with The University of Chicago cloud physics airplane. The flight plan on each of 10 days consisted of three constant level tracks (480 m MSL) each 50–60 km long and oriented approximately perpendicular to the low-level winds. Relative to the St. Louis Metropolitan area, these tracks were upwind, over, and immediately downwind. On each track five to seven membrane filters (MF) were exposed in sequence, each for a duration of 2 min.

Air to be sampled flowed into the cabin by ram pressure through a 7.6 cm diameter tube with inlet ahead of the engines and well-removed from the airplane skin. From this free-flowing supply it was possible to sample simultaneously with the filters and to fill 150-liter capacity metalized-mylar bags for ground-based measurements of CCN with a thermal diffusion chamber and ice nuclei with an expansion chamber.

We used Millipore type AABG04700 filters having a pore size of 0.8 $\mu$m. Air from the sample tube was drawn through the filter by suction from a Venturi. Sample flow was continuously monitored and averaged 66 liters per filter. After collection, the filters were sealed in sterile plastic dishes for subsequent processing using the method described by Stevenson (1968).

The filter processing unit, similar to one described by Langer (1970), directs a gentle flow of cold saturated air in a confined space across the surface of the filter which is independently cooled to a temperature slightly below that of the air. This design, which relies upon molecular diffusion only across the thin convective boundary layer over the filter, is thought to be more effective than one which relies upon diffusion across several millimeters of stagnant air for maintaining saturation at the filter surface during nuclei activation and crystal growth.[2]

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[2] The CPL filter processing device was designed and constructed by Paul Spyers-Duran who also was responsible for processing the filters and analyzing of filter data.

Air flow through the chamber is 3 liters $min^{-1}$ at an average speed of about 2 cm $sec^{-1}$. Temperatures in the chamber are measured with platinum resistance elements and fine thermocouples, both calibrated against an NBS standard. The process air is maintained ice-saturated at −14.9C while the filter is cooled to a top surface temperature of −16.6C. These temperatures subject the nuclei on the filter to an environment just saturated with respect to water at −16.6C. The dew point of air emerging from the humidifier was checked by measuring the temperature of dew formation upon a small mirror previously exposed to cigarette smoke and placed in the normal filter position. Before a filter was placed within the cold chamber, the pores of its lower surface were sealed with petrolatum. The thickness of petrolatum was found hard to control, resulting in slightly different values of $\Delta T$ across the thickness of different filters. Therefore, it was necessary to process filters one at a time and to make fine adjustments in the thermoelectric current to give a repeatable temperature for the upper surface of the filter, as measured by a thermocouple held against the filter by a light, repeatable pressure. Filters were processed without regard to the order in which they were taken, or the location of the samples in order to reduce possible effects of operator bias.

The main disadvantage of the membrane filter technique, especially for studies in polluted urban atmospheres, seems to be the inevitable collection of soluble materials along with the ice nuclei. Soluble materials on the filter surface may cause the humidity on some parts of the filter to be less than saturation during processing, producing the well-known "volume effect." We have sought to overcome this problem by using relatively small sample volumes, by using a forced flow developing chamber, and by using simultaneous CCN data to estimate the Huffman-Vali correction factor.

An unknown, and large, background crystal count can seriously affect the results from small samples. Therefore, we attempted to measure the "background" crystal count on every filter. This was accomplished by modifying the filter holders to block off, and leave unexposed, about one-half of each filter as an annulus surrounding the central "sampling" area.

Fifty-five filters, from four different lots, were processed as blanks to check the consistency of background counts between the "control" and "sample" areas. We found that the numbers of crystals on these unexposed filters ranged from 0 to 49 with an average of 10.8. The outer annular control area usually had the larger number of crystals, possibly as a result of handling. In 37 filters the sample area differed by 2 crystals or less from that predicted by the control; in 45 filters the difference was 4 or less. Translated into probable errors in concentrations, due to this cause, these data mean that for actual concentrations of 1.0 $liter^{-1}$ our values should be within ±0.04, 67% of the time, and ±0.08, 82% of the time. The probable error would be proportionately less (or more) for larger (or smaller) concentrations.

The 150-liter air samples, four per flight, were used for CCN measurements in a thermal gradient diffusion chamber and for ice nucleus measurements with a Bigg-Warner (B-W) expansion chamber. The B-W chamber was operated as described by Crozier (1969) using a wall temperature of −10C and an expansion $\Delta T$ of 10.5C. Minor variations in wall temperature and $\Delta T$ (combined $\approx \pm 0.5$C) have been disregarded in the analysis.

## 3. Results

Ice nucleus and CCN data for each flight are shown in Figs. 1 and 2. Segments of the flight tracks corresponding to filter exposures are indicated along with the ice nucleus concentrations per liter, active at −16.6C. Filters damaged during sampling are indicated by M. The average direction and speed of winds between surface and flight level are indicated for each flight. The dashed line segments, identified as W, X, Y or Z, indicate the locations of air samples used for measurements of CCN spectra and ice nuclei in the B-W expansion chamber. The CCN spectra are expressed in the usual form of $N=cS^k$. Data from the expansion chamber are identified as B-W and represent crystals per liter at an expansion temperature of −20.5C. Cited values are averages from two or three separate expansions from each air sample.

Table 1 summarizes the data on ice nuclei. Flight times are Central Standard, and numbers in parentheses refer to sample size. The wind data suggest that some of the membrane filters on the ends of the "over city" and "downwind" traverses probably did not collect air which had passed over the city. Therefore, these MF were removed from their respective traverses in a separate study resulting in the data identified under "City Plume." Sample size is omitted from the upwind B-W column since there never was more than one air sample on those traverses.

The MF data show an overall average of fewer ice nuclei downwind of the city than upwind and an intermediate value for samples over the city, *viz.* 1.91, 1.60 and 1.43 nuclei $liter^{-1}$, respectively. Moreover, the average downwind concentration was less than the upwind on all but two of the individual days. These two exceptions occurred on the only "easterly" wind days in the sample. We note even larger average differences between upwind (1.91), over city (1.48) and downwind (1.23) MF samples in the City Plume analysis. Again the two easterly wind days are the exceptions.

The B-W data also show an overall average of fewer ice nuclei over and downwind of the city. How-

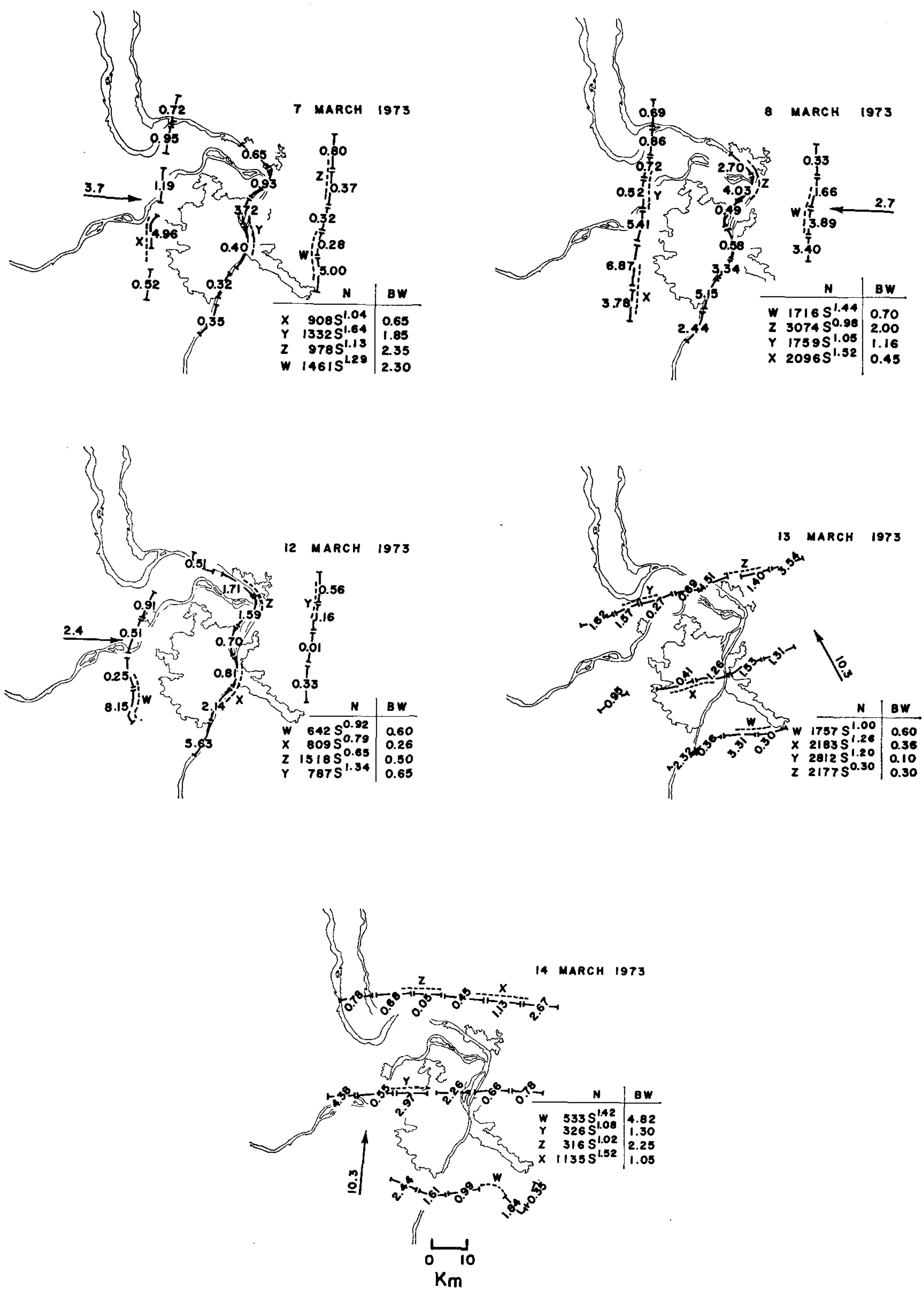


FIG. 1. Individual data points for five flights plotted on map of area around St. Louis, Mo. See text for details.

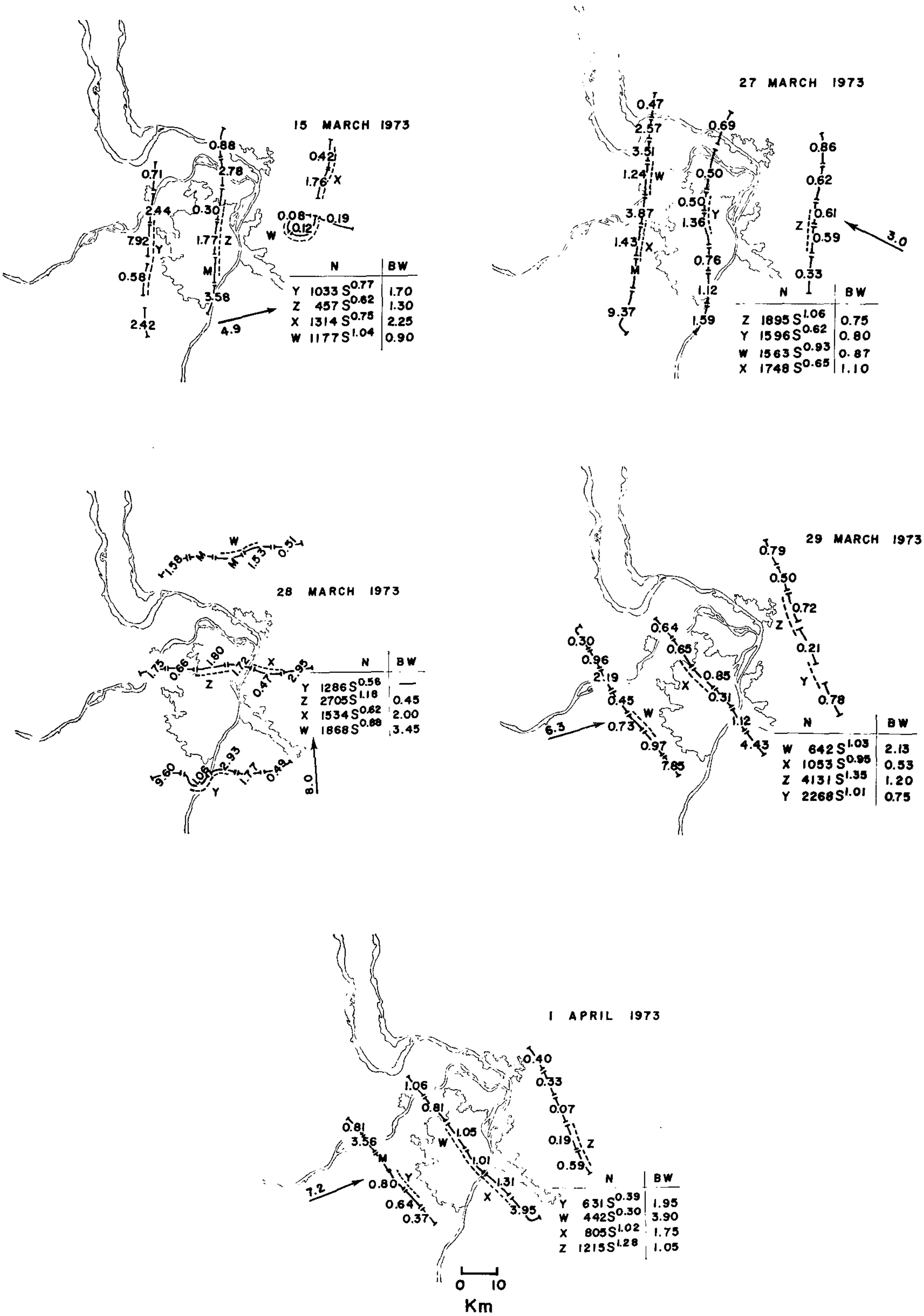


FIG. 2. As in Fig. 1 for five additional flights.

TABLE 1

SUMMARY OF ICE NUCLEUS MEASUREMENTS ST. LOUIS, MO., MARCH, 1973.

| | | | MEMBRANE FILTER ICE NUCLEI - No. per Liter -16.6 C | | | | | | | B-W ICE NUCLEI No. per Liter -20.5 C | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Flight | Wind | All Filter Data | | | City Plume | | Corrected | | | | |
| Date | Times | deg-mps | upwind | over | downwind | over | downwind | up | down | up | over | downwind |
| Mar 7 | 1455-1611 | 275-3.7 | 1.67 (5) | 1.06 (6) | 1.35 (5) | 1.34 (4) | 1.35 (5) | 2.30 | 1.79 | 0.65 | 1.85 (1) | 2.32 (2) |
| 8 | 0943-1157 | 80-2.7 | 2.32 (4) | 2.68 (7) | 2.69 (7) | 2.72 (6) | 3.03 (6) | 3.70 | 4.60 | 0.70 | 2.00 (1) | 0.80 (2) |
| 12 | 0928-1129 | 290-2.4 | 2.46 (4) | 1.87 (7) | 0.52 (4) | 1.38 (4) | 0.52 (4) | 3.78 | 0.59 | 0.60 | 0.38 (2) | 0.65 (1) |
| 13 | 1019-1153 | 155-10.3 | 1.57 (4) | 1.10 (5) | 1.51 (7) | 1.08 (3) | 1.09 (5) | 2.22 | 2.20 | 0.60 | 0.36 (1) | 0.20 (2) |
| 14 | 1014-1156 | 185-10.3 | 1.45 (5) | 1.93 (6) | 0.96 (6) | 1.96 (3) | 0.58 (4) | 1.88 | 1.17 | 4.82 | 1.30 (1) | 1.65 (2) |
| 15 | 0908-1031 | 205-4.9 | 2.81 (5) | 1.86 (5) | 0.51 (5) | 2.11 (4) | 0.51 (5) | 4.66 | 0.59 | 1.70 | 1.30 (1) | 1.58 (2) |
| 27 | 1443-1612 | 120-3.0 | 0.60 (5) | 0.93 (7) | 3.21 (7) | 0.82 (6) | 2.18 (6) | 0.73 | 5.89 | 0.75 | 0.80 (1) | 0.98 (2) |
| 28 | 1058-1123 | 170-8.0 | 3.17 (5) | 1.56 (6) | 1.21 (3) | 1.56 (6) | 1.21 (3) | 5.66 | 1.63 | -- | 1.22 (2) | 3.45 (1) |
| 29 | 0901-1029 | 270-6.3 | 1.92 (7) | 1.33 (6) | 0.60 (5) | 0.71 (5) | 0.55 (4) | 2.70 | 0.75 | 2.13 | 1.20 (1) | 0.97 (2) |
| Apr 1 | 0917-1041 | 250-7.2 | 1.24 (5) | 1.53 (6) | 0.32 (5) | 1.05 (5) | 0.32 (5) | 1.57 | 0.36 | 1.95 | 2.82 (2) | 1.05 (1) |
| | | TOTALS | 49 | 61 | 54 | 46 | 47 | -- | -- | 9 | 13 | 17 |
| | | AVERAGES | 1.91 | 1.60 | 1.43 | 1.48 | 1.23 | 2.92 | 1.96 | 1.54 | 1.36 | 1.30 |

ever, this trend is supported by only 5 of 9 days having both upwind and downwind samples.

Our purpose now is to examine the evidence to see whether this tendency for lower downwind concentrations may be due to sampling fluctuations or to an effect of the city in deactivating ice nuclei passing overhead.

In examining the individual filter values, we found that the averages tend to be weighted by several relatively large values. Therefore, we have used the Wilcoxon-Mann-Whitney (WMW) two-sample rank test to check for significance of the differences between upwind and downwind samples.

Application of the WMW to the MF data for individual days shows only three with $P<0.05$. These are 15 and 27 March and 1 April. Of these, 27 March had a SE wind and gave downwind increases, while the other two indicate downwind decreases. Taking the 49 upwind and 54 downwind MF as a single sample, the WMW gives $P=0.04$ (one-sided), while the 49 upwind and 47 City Plume downwind MF give $P=0.014$. These values, together with the 8 of 10 support from daily averages, gives strong evidence for rejecting the conclusion that the upwind and downwind samples came from the same population. The downwind and upwind median values were 0.42 and 0.58 nuclei liter$^{-1}$ for a ratio of 0.72 compared with 0.75 ratio of the arithmetic averages.

The B-W samples were tested only as a single sample because of the small sample size. The WMW applied to 9 upwind and 17 downwind samples gave $P>0.4$, giving no reason to reject the null hypothesis of equal medians.

Both MF and B-W data showed a tendency for the largest counts to occur on the south and west sides of the city (Figs. 1 and 2). We also noted earlier that the two days with easterly winds found the largest counts on the downwind traverse (west of the city). We rule out the possibility that air masses with winds from south through west have larger than average nucleus counts because: (i) the two easterly wind days also had the highest counts south and west of the city; (ii) the traverses across the city, and north to east of the city on south to west wind days, did not show a tendency for abnormally high counts on the ends (i.e., outside the city plume); and (iii) individual high count filters on the south and west sides of the city were usually mixed in with several of much lower counts indicating a local source rather than an air mass property.

Expanding this last point we observe that if there were local sources for ice nuclei on the south and west sides of the city, the two easterly wind days should be set aside in an analysis aimed at deducing any urban effect on nuclei. The WMW test applied to the 40 upwind and 40 downwind MF from days with winds between 155° and 290° give $P<0.0001$, which, along with 8 of 8 individual days with lower downwind counts, gives very strong evidence for an urban effect causing a decrease in ice nuclei as measured on MF as air crossed the city. Estimates of the magnitude of this effect can be obtained from the data. The median downwind and upwind values are 0.30 and 0.48 nuclei liter$^{-1}$, for a ratio of 0.62. The arithmetical average values are 2.03 and 0.70 for a ratio of 0.34.

The only known reason for questioning whether these data signify a real decrease in MF ice nuclei is associated with the MF "volume-effect" mentioned earlier. Mossop and Thorndyke (1966), Lala and Jiusto (1972), and Huffman and Vali (1973) discuss the effect of soluble aerosols, collected with the ice nuclei on MF, in decreasing the number of ice nuclei activated. It has already been established that the St. Louis area is a prolific source of CCN (Fitzgerald and Spyers-Duran, 1973; Spyers-Duran, 1972; Braham, 1974). Data on CCN accompanying these particular ice nucleus collections are given in Figs. 1 and 2. Huffman and Vali (1973) propose a method for arriving at a correction factor by which the MF should be adjusted to allow for the effects of the soluble aerosol. Although they urge caution in applying their correction to other data, at this time there is no obviously better approach to this problem with our data. We have computed the Huffman-Vali $E$ factor for each of the daily average upwind and downwind MF nuclei counts.[3] The results are given in Table 1. It is clear that this adjustment does nothing to negate the evidence for an urban effect in decreasing MF-type ice nuclei.

During the course of this study several pairs of MF measurements were obtained upwind and downwind of a petroleum refinery, five of seven indicating nucleus decreases. Nine pairs upwind–downwind of a steel smelter showed eight out of nine with downwind decreases. Six of seven B-W pairs showed nucleus increases downwind of the refinery. Upwind–downwind of the steel mill four B-W split evenly.

## 4. Comparison between simultaneous MF and B-W nuclei concentrations

During this sample period we obtained 39 measurements of B-W ice nucleus concentrations which can be compared with MF samples taken at the same times and places. The correlation between them is $-0.13$. The average concentration of nuclei on MF (1.64 liter$^{-1}$) was quite similar to the average seen by the B-W chamber at an expansion temperature of $-20.5$ (1.46 liter$^{-1}$). If one uses expansion chamber nuclei temperature-spectra reported by Kline (1963) or Bourquard (1963) to "normalize" the B-W counts to the temperature of the filters, they would be reduced by about an order of magnitude. Thus, not only is there low correlation between simultaneous samples using the two techniques, but the values obtained with the B-W chamber are about an order of magnitude less than with the filters. These differences between MF and B-W ice nucleus measurements are not particularly surprising, but they do indicate again the need for caution in interpreting various types of ice nuclei data.

## 5. Conclusions

During March 1973 ice nucleus concentrations measured by the membrane filter technique were found to be lower downwind than upwind of the St. Louis Metropolitan area. There is strong statistical support for this decrease being a real effect of some agent of the city which deactivates natural nuclei of the types detected by the filter technique.

There is substantial evidence for intense local sources for ice nuclei on the south and west sides of St. Louis. The study does not suggest the nature of these sources. Simultaneous samples using the filter technique and the Bigg-Warner expansion temperature show no correlation and almost an order of magnitude difference in concentrations. The expansion chamber data do not support an urban effect for decreasing ice nuclei.

[3] In a personal communication Prof. Vali has indicated an arithmetic error affecting the lower abscissa of their Fig. 7. They plan a corrigendum.

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