

NOTES

**Relationships among Lead, Iodine, Trace Metals and Ice Nuclei
in a Coastal Urban Atmosphere**

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17 November 1978 and 18 July 1979

ABSTRACT

Particulate lead, aluminum, sodium, vanadium, manganese and iodine, vapor phase iodine and ice nuclei were measured simultaneously in Providence, Rhode Island, over a period of one year. Interrelationships found were governed primarily by the physical properties of the aerosol. Weak positive correlations were observed between lead and ice nuclei. An argument is given using lead as an indicator of the aerosol surface area maximum, or that fraction of the aerosol which contains the greatest number of potential ice nucleating sites. Ice nucleus concentrations appeared to be controlled by large-scale air mass advection to the site studied.

1. Introduction

A study was undertaken to determine whether a relationship existed between ambient lead, iodine and ice nuclei in an urban atmosphere. Ambient concentrations of aluminum, sodium, vanadium and manganese were determined to aid in the interpretation of the data. Previous studies (Schaefer, 1966, 1968a,b, 1969, 1978; Moyers and Duce, 1974; Montefinale *et al.*, 1971; Hogan, 1967; Morgan, 1967; Parungo and Rhea, 1970) have suggested that ice nuclei produced by the reaction of lead from automobile exhaust with iodine (I_2) vapor may have an important effect in inadvertent weather modification. Others (Grant and Corrin, 1973) have shown the lead additives are not important in the production of potential ice nuclei from automobile exhaust and that formation of PbI_2 will not occur in the atmosphere.

2. Sampling and analytical procedures

Samples were collected over a one-year period in downtown Providence, Rhode Island, beginning October 1972 and represent a cross section of different atmospheric conditions. Fig. 1 shows the relative location of the sampling site. Pollutant concentrations and meteorological parameters were also determined to aid in the interpretation of the data. Each sample was representative of a 4 h time period. Samples for ice nuclei determination were collected using 47 mm Millipore Type HA filters taken at the beginning, middle and end of the period.

Each Millipore filter sample was collected for 5 min at $\sim 20 \ell \text{ min}^{-1}$ flow rate. Samples for lead and particulate iodine determinations were collected for 4 h using $0.45 \mu\text{m}$ pore size Nuclepore filters. The particulate iodine filter was followed by an activated carbon trap which was used to collect the total vapor phase iodine.

Lead concentrations were determined by atomic absorption spectrophotometry. Both the filter and the carbon trap were analyzed for iodine by neutron activation analysis and gamma ray spectroscopy, using a combination of a modification of the procedure as described by Duce and Winchester (1965) and a direct nondestructive irradiation and counting technique. Vanadium, manganese, sodium and aluminum were simultaneously determined from the nondestructive portion of the gamma ray analysis technique.

Ice nuclei were determined by the Stevenson (1968) method using a modified thermal diffusion chamber (Gagin and Aroyo, 1969) available from Meeda Scientific Instrumentation, Ltd., Israel. The samples were run at nominal water saturation at -17°C . The ice nucleus sample volumes were generally less than 100ℓ . The results are expressed as concentrations determined directly from the observed ice crystal count and the measured volume. No attempt was made to correct for diffusion chamber size as mentioned by Justo *et al.* (1976), volume effect, or hygroscopic particle concentration (Huffman and Vali, 1973). The first effect was a constant within the analysis, and the latter two

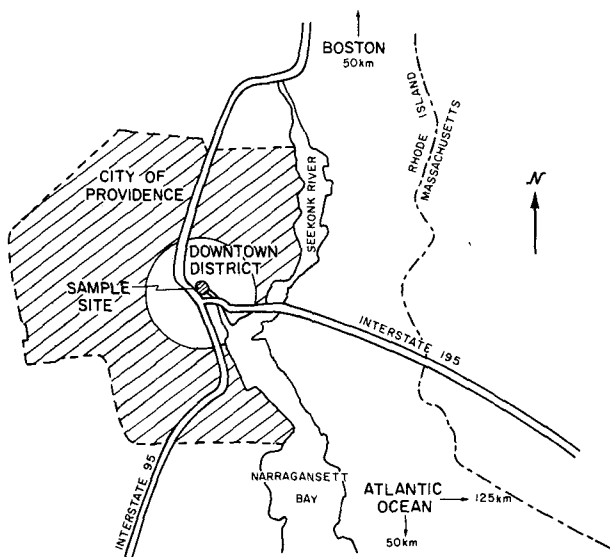


FIG. 1. Location of the sampling site relative to the city of Providence, RI.

effects are considered to be minimal due to the small sample volumes.

3. Results

a. Particulate lead and ice nuclei

Fig. 2 is a plot of lead concentration versus wind direction. Comparing Figs. 1 and 2, it appears that the factor most important in determining the lead concentration was the coincidence of the azimuth of the wind direction and the axes of the major interstate highways radiating from the sampling site. Fig. 3 shows the relation between ice nuclei and wind direction. The correlation coefficient between lead and ice nucleus concentration was +0.320. The correlation coefficient between the lead enrichment factor and ice nucleus concentration was found to be -0.226. The enrichment factor is defined by

$$EF_X(Al, rock) = (X/Al)_{aerosol} / (X/Al)_{rock},$$

using aluminum as an indicator of crustal aerosol and average crustal rock concentrations as given by Mason (1966) as the reference material. Using carbon monoxide as an indicator of the buildup of auto emissions, the correlation found with ice nuclei was +0.104.

It has been reported that the primary lead compound in fresh auto exhaust is $PbBrCl$. As decomposition occurs with aging of the aerosol in the atmosphere, lead oxides, sulphates, carbonates, oxysulphates and oxycarbonates are formed (Ter-Haar and Bayard, 1971). None of these compounds are known to be good ice nucleants. It is impossible from chemical equilibria considerations to form

PbI_2 , a good ice nucleant, from any of the above lead compounds in the presence of I_2 or I^- .

It is apparent that no strong relationship exists between the local lead emissions of automobiles and the ice nuclei activity found for Providence. This suggests that lead emissions and/or auto exhaust may not play an important part in ice nucleus production at this particular location.

b. Vapor phase iodine and ice nuclei

Fig. 4 is a plot of both vapor phase and particulate iodine concentration versus wind direction. The correlation coefficient between ambient vapor phase iodine and ice nucleus concentration was -0.394. The primary species of iodine in the atmosphere is probably not the elemental form I_2 (Rahn *et al.*, 1976). It is most likely found as an organic species, perhaps CH_3I , which may not react rapidly with aerosols to form ice nuclei.

Interpretation by Moyers *et al.* (1971) of estimates by Schaefer (1966) indicates that 1 ng m^{-3} of gaseous I_2 in polluted air should activate all the lead particles in the atmosphere since only a surface site is required on the aerosol. A bulk chemical reaction is not necessary. This study does not indicate that the dominant vapor phase iodine species is I_2 .

Fig. 4 shows larger vapor phase iodine concentrations associated with air masses which are of marine origin; i.e., air masses which arrived at the collection site from the Atlantic Ocean sector. This is in accordance with recent findings (Rahn *et al.*, 1976) that air masses with recent marine histories have a larger concentration of total vapor phase iodine. The ratio of mean vapor phase iodine concentration in

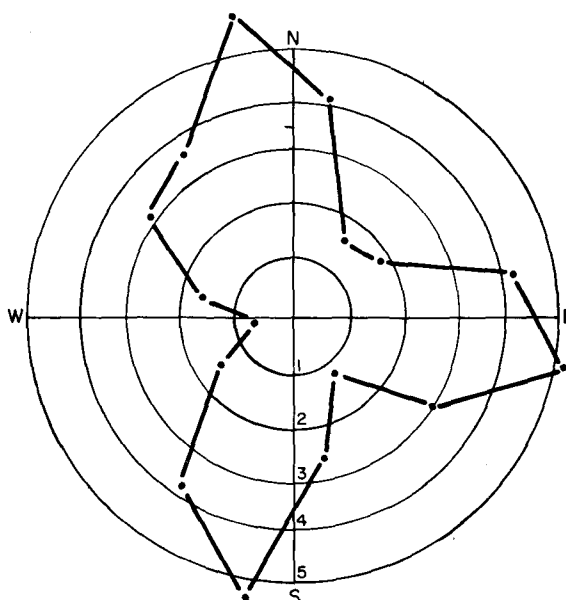


FIG. 2. Lead versus wind direction, concentrations in $\mu\text{g m}^{-3}$.

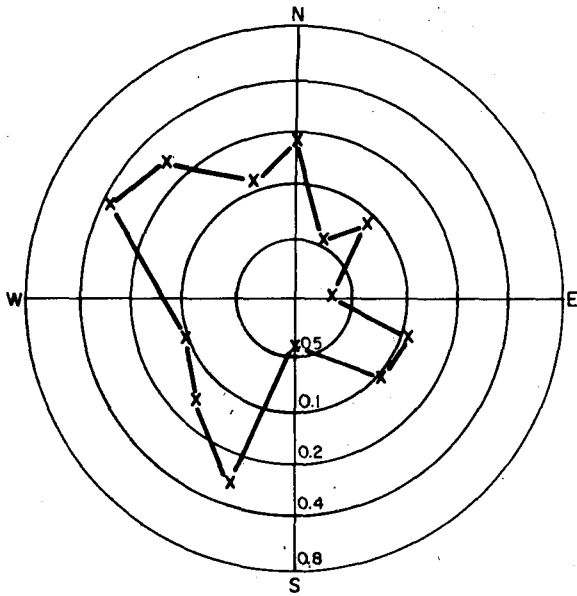


FIG. 3. Ice nuclei versus wind direction, concentrations in nuclei liter⁻¹.

the east versus the west sector is 3.1. Thus increases in the ambient concentration of vapor phase iodine, whatever the species, do not increase ice nucleus concentrations.

The sampling site is located essentially at the point at which marine air masses first encounter pollution sources. Since CH₃I is photodissociated in the atmosphere and could provide a more reactive source of iodine such as I₂, it is possible that the reaction necessary to produce PbI₂ would occur further downwind of the sampling site. However, as indicated above, it is unlikely that elemental lead exists in the aerosol.

c. Particulate iodine and ice nuclei

If iodine is important in the formation of an ice nucleus, then a relationship should occur between the particulate iodine and ice nuclei concentrations. No direct correlation was observed. The correlation coefficient between particulate iodine and ice nuclei was -0.107. The correlation observed between particulate iodine and particulate lead was +0.565 at the 3% level of significance. Thus, although there is some association indicated between particulate lead and iodine, there is little evidence for this being associated with ice nucleus formation.

Fig. 4 shows the relationship between particulate iodine and wind direction. It is apparent that particulate iodine has a source to the east, or in the marine sector. The sea is known to be a source of particulate iodine (Winchester and Duce, 1966; Duce *et al.*,

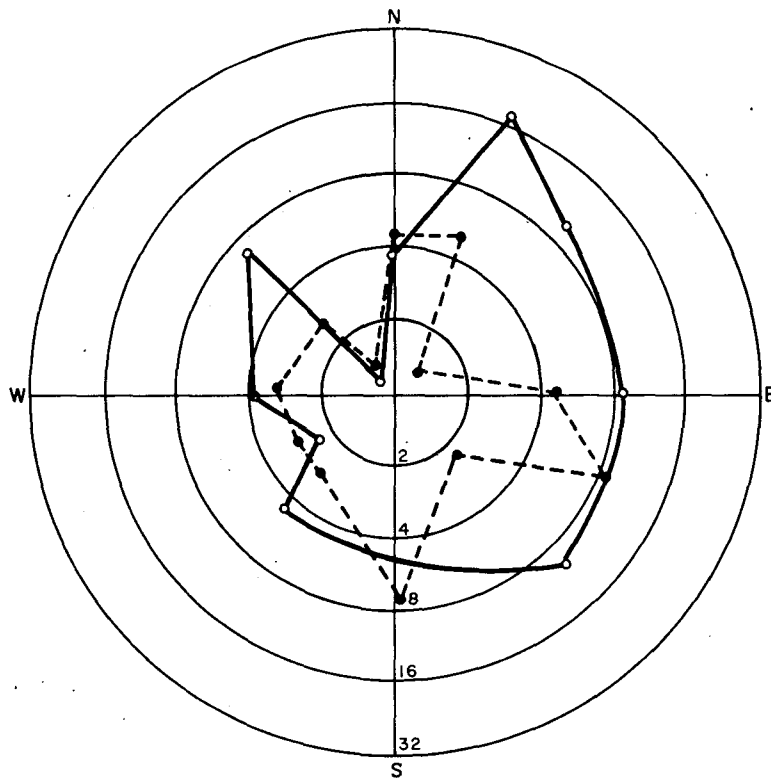


FIG. 4. Particulate iodine (dashed line) and vapor phase iodine (solid line) versus wind direction, concentrations in ng m⁻³.

1965). The ratio of mean particulate iodine concentration in the east versus the west sector is 1.6.

Studies at Barrow, Alaska (Radke *et al.*, 1976) showed a negative correlation of -0.219 between sodium containing particles and ice nuclei determined at -20°C . This present study showed a correlation coefficient of -0.223 between total particulate sodium and ice nuclei.

4. Discussion and conclusions

From this study no strong indicators could be found which would aid in determining specific sources of ice nuclei. However, indirect evidence suggests that the submicron portion of the aerosol which dominates the total aerosol surface area is the important fraction for ice nucleation. No inter-relationship between lead or iodine and ice nuclei was observed. In a complex aerosol environment such as an urban region, only very strong sources or non-sources of ice nuclei can be found. As Fig. 3 shows, the strongest source of ice nuclei occurred to the northwest and southwest of the study location. These directions, in general, are continental air mass source regions.

Continental aerosol from this sector should have maxima in the volume distribution in the submicron size fraction (the fine particle mode) due to the coagulation process as well as in the coarse particle mode of the aerosol near $10\ \mu\text{m}$ radius. This aerosol should have a greater total surface area than that of a fresh marine aerosol. Typical continental aerosols have 10–20 times the surface area of a marine aerosol. The marine aerosol has a peak in the surface area distribution which is typically around $2\ \mu\text{m}$ radius, whereas that of the continental aerosol occurs near $0.2\ \mu\text{m}$ radius.

The ice nucleating properties of an aerosol are associated with its surface and its bulk composition. It should be expected that an aerosol with a greater surface area relative to another aerosol of similar composition should, in general, have greater ice nucleating potential. The composition of the aerosol must also be taken into account. It should be possible to use the aerosol trace metal composition to identify the aerosol type, and to relate its ice nucleating activity to the known physical properties of such an aerosol and the importance of its source to the ice nucleus concentration.

Fig. 5 presents a typical continental or urban aerosol volume and surface area distribution (Whitby *et al.*, 1972). Indicated on this plot are the mass median diameters (MMD) for the five trace metals used in this study as compiled by Rahn (1976). Correlation coefficients for each metal versus ice nucleus concentration and total suspended particulates (TSP) from this study are also listed. If the trace metal data are used as indicators of the aerosol in general, a few points can be made.

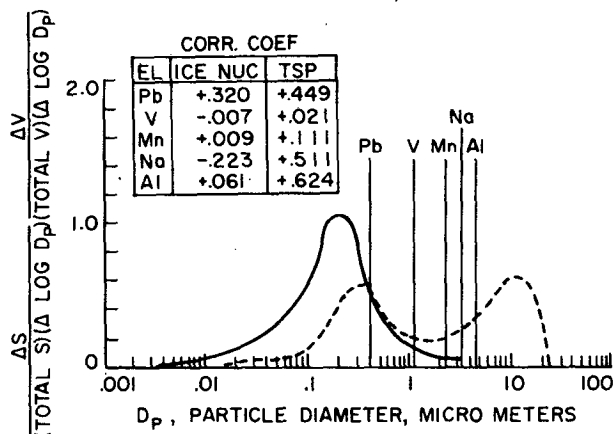


FIG. 5. Aerosol surface area (solid line) and volume (dashed line) distributions from Whitby *et al.*, 1972, with mass median diameters for the trace metals from Rahn (1976). Correlation coefficients between trace metals, TSP and ice nucleus concentrations are from this study. See text for discussion.

Based on Fig. 5, a stronger relationship should exist between Pb, Na, Al and TSP than between V, Mn and TSP. This is apparent in this study where the correlation coefficients between the former were $+0.449$, $+0.511$, and $+0.624$, respectively. The correlation for Al was greater than that for Na as one would expect from the relative position of the two elemental MMD's and the maximum of the coarse particle mode of the aerosol volume distribution. Finally, the relationships of the masses of V and Mn to TSP show weak positive correlations relative to the other metals, as would be expected. Thus, indirect evidence suggests the aerosol studied here has a bimodal volume distribution as shown in Fig. 5, and therefore should have a similar surface area distribution.

Lead is almost entirely found within the fine particle mode. Therefore it is also a good indicator for the size fraction of the aerosol which contains most of the aerosol surface area. Thus lead, the only trace metal which had a significant positive correlation with ice nucleus concentrations, indicates the importance of the submicron size fraction of the aerosol in ice nucleation. Recent work by Cooper (1976) indicated that ice nuclei in a continental aerosol were primarily found to be less than $0.2\ \mu\text{m}$ in diameter.

Sodium, a metal typically used as a tracer for marine aerosol, has a negative correlation with ice nuclei concentration for several reasons. The marine aerosol has a significantly smaller total surface area than that of a continental or pollution aerosol. Marine air masses in general do not have high ice nucleus concentrations and are considered to be relatively "clean" in this region. Sodium is primarily associated with the coarse particle mode of

the aerosol and is far removed from the surface area maximum.

Aluminum, which is a good indicator of crustal aerosol, displayed no apparent trend in association with ice nuclei activity of the aerosol. Crustal aerosol is considered to be a relatively good natural ice nucleant (Mason, 1971). Of the five metals determined, Al has the largest MMD. The Al mass is primarily associated with the coarse particle mode and has little contribution to the total aerosol surface area. Therefore, even though a crustal aerosol has the potential of being an ice nucleant, the mass bears no relation to the aerosol fraction most active in nucleating ice.

Vanadium and manganese have a significant pollution source. Their MMD's are located at the minimum between the coarse and fine particle modes of the aerosol, well removed from the region of the surface area maximum. Thus little or no correlation was observed between ice nucleus concentration and these metals.

The major conclusion from this study is that the greatest effect on the ice nucleus concentration in Providence, Rhode Island, is due to the difference in the ice nuclei concentration existing in the contrasting air masses of continental and marine origin which are advected to this site. In general, this is consistent with the findings of other investigators, with the continents being the primary source of ice nuclei due to crustal weathering and/or certain activities of man. It is possible to use the bulk aerosol trace metal data as indicators in studies of ice nuclei to aid in determining the large-scale sources of ice nuclei.

To determine what aerosols are directly playing a role in the nucleation process, single particle analysis of aerosols in ice crystals formed in the laboratory and nature is necessary. Studies using this technique are now being undertaken.

Acknowledgments. This research was performed under National Science Foundation Grants GA-31918 and 75-23725 as part of research on the atmospheric chemistry of the halogens sponsored by the NSF Atmospheric Sciences Section. Special thanks go to Professor Lewis Grant and Dr. Dennis Garvey at Colorado State University for their helpful suggestions and use of their facilities, and to Dr. Ian Fletcher who assisted in the data collection and analysis.

REFERENCES

- Cooper, W. A., 1976: Ice nucleus measurements using a Stober centrifuge. *Third Int. Workshop Ice Nucleus Measurements*, Laramie, 19 May–6 June 1975, National Science Foundation, 63–74.
- Duce, R. A., and J. W. Winchester, 1965: Determination of iodine, bromine and chlorine in atmospheric samples by neutron activation. *Radiochim Acta*, **4**, 100–104.
- , —, and T. W. Van Nolin, 1965: Iodine, bromine and chlorine in the Hawaiian marine atmosphere. *J. Geophys. Res.*, **70**, 1775–1779.
- Gagin, A., and M. Aroyo, 1969: A thermal diffusion chamber for the measurement of ice nucleus concentrations. *J. Rech. Atmos.*, **4**, 115–122.
- Grant, L. O., and M. L. Corrin, 1973: Raw and iodine treated automobile exhaust as a source of ice nuclei. *J. Wea. Mod.*, **5**, 238–248.
- Hogan, A., 1967: Ice nuclei from direct reaction of iodine vapor with vapor from leaded gasoline. *Science*, **158**, 800.
- Huffman, P., and G. Vali, 1973: The effect of vapor depletion on ice nucleus measurements with membrane filters. *J. Appl. Meteor.*, **12**, 1018–1024.
- Jiusto, J., G. Lala and J. Zamurs, 1976: Filter measurements of ice nucleus concentrations and selected comparisons. *Preprints Int. Conf. Cloud Physics*, Boulder, Amer. Meteor. Soc., 53–56.
- Mason, B., 1966: *Principles of Geochemistry*, 3rd ed. Wiley, 329 pp.
- Mason, B. J., 1971: *The Physics of Clouds*. Clarendon Press, 671 pp.
- Montefinale, A., E. G. Gori and H. M. Papee, 1971: An evaporator of iodine for purposes of weather control. *Pure Appl. Geophys.*, **91**, 211–217.
- Morgan, G. M., 1967: Technique for detecting lead particles in air. *Nature*, **213**, 58–59.
- Moyers, J. L., and R. A. Duce, 1974: The collection and determination of atmospheric gaseous bromine and iodine. *Analytica Chimica Acta*, **69**, 117–127.
- , W. H. Zoller and R. A. Duce, 1971: Gaseous iodine measurements and their relationship to particulate lead in a polluted atmosphere. *J. Atmos. Sci.*, **28**, 95–98.
- Parungo, F., and O. Rhea, 1970: Lead measurement in urban air as it relates to weather modification. *J. Appl. Meteor.*, **9**, 468–475.
- Radke, L., P. Hobbs and J. Pinnons, 1976: Observations of cloud condensation nuclei, sodium containing particles, ice nuclei, and the light scattering coefficient near Barrow, Alaska. *J. Appl. Meteor.*, **15**, 982–995.
- Rahn, K. A., R. D. Borys and R. A. Duce, 1976: Tropospheric halogen gases: Inorganic and organic components. *Science*, **192**, 549–550.
- , 1976: The chemical composition of the atmospheric aerosol. Tech. Report, Graduate School of Oceanography, University of Rhode Island, 265 pp.
- Schaefer, V. J., 1966: Ice nuclei from automobile exhaust and iodine vapor. *Science*, **154**, 1555–1557.
- , 1968a: Ice nuclei from auto exhaust and organic vapors. *J. Appl. Meteor.*, **7**, 148–149.
- , 1968b: The effect of a trace of iodine on ice nucleus measurements. *J. Rech. Atmos.*, **3**, 181–183.
- , 1969: The inadvertent modification of the atmosphere by air pollution. *Bull. Amer. Meteor. Soc.*, **50**, 199–206.
- , 1978: Is something happening to our supply of supercooled clouds? *J. Wea. Mod.*, **10**, 1–3.
- Stevenson, C. M., 1968: An improved Millipore filter technique for measuring the concentrations of freezing nuclei in the atmosphere. *Quart. J. Roy. Meteor. Soc.*, **94**, 35–43.
- Ter Haar, G. L., and M. A. Bayard, 1971: Composition of airborne lead particles. *Nature*, **232**, 553–554.
- Whitby, K. T., R. B. Husar and Y. H. Liu, 1972: The aerosol size distribution of Los Angeles smog. *J. Colloid Interface Sci.*, **39**, 177–204.
- Winchester, J. W., and R. A. Duce, 1966: Coherence of iodine and bromine in the atmosphere of Hawaii, northern Alaska, and Massachusetts. *Tellus*, **14**, 1–18.