Biogenic Ice Nuclei: Part I. Terrestrial and Marine Sources

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(Manuscript received 24 October 1975, in revised form 31 March 1976)

ABSTRACT

Decayed plant leaf litters from North America, Europe and Asia have been found to contain copious numbers of ice nuclei, some active at −4°C. The abundance of nuclei in a litter was noted to vary according to the climate of the plant's origin; litters from tropical, A-type climates (according to the Köppen classification) contain fewer ice nuclei (10^3 g^{-1} active at −10°C) than litters from mid-latitude, C-type climates (10^5 g^{-1} active at −10°C) which in turn contain fewer nuclei than litters from high-latitude, D-type climates (10^9 g^{-1} at −10°C). The rate of release of freezing nuclei to the atmosphere from *in situ* litters from D-type climates was determined experimentally: the flux of nuclei active at −12°C was found to be 10^1–10^3 cm^{-2} day^{-1} during daylight hours.

Active ice nuclei also have been found in seawaters rich in phytoplankton; seawaters devoid of plankton are poor sources of ice nuclei. Some of these nuclei are active at temperatures around −4°C and concentrations reach up to 10^7–10^8 nuclei at −10°C per gram of plankton.

Using numerous measurements from around the globe, atmospheric ice nucleus concentrations, and also freezing nucleus concentrations in rainfall, were shown to exhibit a climatic dependence similar to that of biogenic nuclei sources at the surface. This correlation suggests that large proportions of atmospheric ice nuclei are possibly of biogenic origin.

1. Introduction

The previous several decades of investigations of atmospheric ice-forming nuclei have provided a number of clues regarding the composition and origin of the nuclei. Albeit, the evidence in each case is tenuous and the question of origin of the nuclei must still be regarded as open. A new suggestion, and some supporting evidence, will be put forth in this paper and its companion (Part II).

While the literature on ice nuclei is quite voluminous it is possible to group the main ideas concerning origin into the following categories.

1) The possibility of extraterrestrial, meteoritic origin for atmospheric ice nuclei has been considered, and dismissed, by Findeisen (1938). Bowen (1953) renewed the suggestion, based on climatological data showing rainfall peaks corresponding (with a time lag) to meteorite showers. Tests by Schaefer (1957) and by Gokhale and Gould (1969) indicated that meteoritic materials are not good sources of ice nuclei at temperatures warmer than −15°C. On the other hand, Bigg and Giutronich (1967) found that aerosolized meteoritic materials are quite effective as ice nuclei.

2) A large number of laboratory tests revealed that inorganic soil particles (mainly clays) are good ice nucleators, though mostly at temperatures colder than −15°C. Strong indication that clay particles may provide large proportions of the atmospheric ice nuclei was given by Kumai (1961) and others, who found clay particles at the centers of most snowflakes.

3) Rosinski and Parungo (1966) found by laboratory experiments that natural plant oils could produce ice nucleation at temperatures of −8°C and colder, and that some terpenes were even more active. Experiments with two species of coniferous trees revealed no noteworthy production of ice nuclei. (However, reaction products of plant oils with silver iodide proved to be abundant ice nucleus sources.)

4) A maritime source for ice nuclei has been suggested by Brier and Kline (1959) and Battan and Riley (1960). On the other hand, based on simultaneous ice nucleus measurements at three widely separated sites in Washington State, Hobbs and Locatelli (1970) report that the ocean was a poor source of nuclei.

5) Measurements have been reported of high concentrations of atmospheric ice nuclei above and downwind of some specific anthropogenic sources (Soulage,

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[2] The National Center for Atmospheric Research is sponsored by the National Science Foundation.

1958, among the first), but the recent data of Bigg and Stevenson (1970) and of Bigg (1973) show no evidence that anthropogenic aerosols contribute significantly to the global population of atmospheric ice nuclei.

More detail on atmospheric ice nuclei can be found in the reviews of Bigg (1960), Mossop (1963) and Pruppacher (1973), and in the standard cloud physics texts.

A common difficulty with the ice nucleus sources discussed above is that none appears to be capable of producing high concentrations of nuclei active at temperature warmer than −10°C. Yet, the existence of such nuclei is commonly evidenced by the occurrence of ice crystals in clouds as warm as −5°C. Also, the better ice nucleants which have been identified in the laboratory have limited terrestrial distribution and are absent from marine environments.

The suggestion that materials of biological origin may be acting as atmospheric ice nuclei first emerged from the finding by Soulage (1957) that bacterial cells can become centers of ice crystals in a cloud chamber. Vali (1968) found that natural soils containing large fractions of organic materials were considerably better sources of freezing nuclei than the basic clay constituents of those soils. A plausible explanation for this latter fact was given in our 1972 paper (Schnell and Vali, 1972), which showed that copious numbers of organic freezing nuclei, active at temperatures as warm as −4°C, were produced during the decomposition of naturally occurring vegetation. The ubiquity of such nuclei was established by finding active freezing nuclei in plant litters collected around the world (Schnell and Vali, 1973). Furthermore, organic freezing nuclei active at −3°C have been recently observed in association with marine plankton (Schnell and Vali, 1975). Parts I and II of this paper summarize our current knowledge about biogenic nuclei.

Briefly, the point of Part I is that ice nuclei are available, on a worldwide basis, from decaying vegetation in terrestrial areas and from some component of the plankton biomass in marine environments. In Part II it is shown that the production of ice nuclei in decaying vegetation can be bacterially mediated and the potential is demonstrated for a bacterially-associated very active ice nucleant source (nucleation at temperatures close to −1°C).

An important caveat is necessary in any discussion of atmospheric ice nucleation. Because of well-known difficulties associated with the measurements of ice nuclei, interpretation of results is by no means straightforward. Relative values from a single instrument are most likely to be correct, though there are potential hazards even there, especially with respect to the specifications of relevant experimental conditions. For this reason, atmospheric ice nucleus measurements are used in this paper only for comparative purposes, and we refrain from attempts to reconcile in detail our observations with the large body of published material. The majority of measurements described in this paper utilized a technique which possesses well-documented reproducibility, but is known to simulate only one of the possible modes of activity in the atmosphere. These problems of ice nucleus measurements undoubtedly impart some tentativeness to the results; it can only be hoped that future research will help to clarify our current dilemmas.

2. Methods and materials

a. Terrestrial plant matter collection

The collection sites for plant litter were generally selected for their remoteness from anthropogenic sources. Collection consisted of gathering fallen leaves and/or decaying litter from the uppermost layers of ground and inserting the materials into inert plastic bags. Individual samples generally weighed between 100 and 300 g. The samples were stored at ambient temperatures.

b. Aerosol capture

A liquid scrubber was used to capture in water the natural aerosol products of decaying vegetation. An open-bottomed 1 m^3 tent was mounted above plant litters and the aerosols were drawn through a 20-gallon plastic cylinder by a vacuum pump. While passing through the cylinder, the aerosol was subjected to a fine-falling water spray, the water being continuously recirculated. The system was generally operated from 6–18 h per experiment. Subsequently, the material collected in the water was tested for freezing nucleus content.

c. Marine sample collection

Samples of ocean water were collected by filling 500 cm^3 sealable plastic bottles from within $\frac{1}{2}$ m of the surface. Masses of indigenous plankton and related organic matter were obtained by sieving the top 1 m layer of water with a standard 20 μm plankton net. When the net pores became saturated with micro-organisms and associated organic detritus, the captured material was scraped into small, chemically inert plastic bags. Sample weight generally varied between 10 and 100 g for a haul distance of about 1500 m. The samples were stored frozen. Some samples were tested within a few hours after collection and again after storage; no differences could be detected.

d. Precipitation collection

Precipitation at the earth's surface was obtained by exposing previously sealed and sterilized plastic bags during a precipitation event. At the end of the sampling period the collected precipitation (from a few cubic

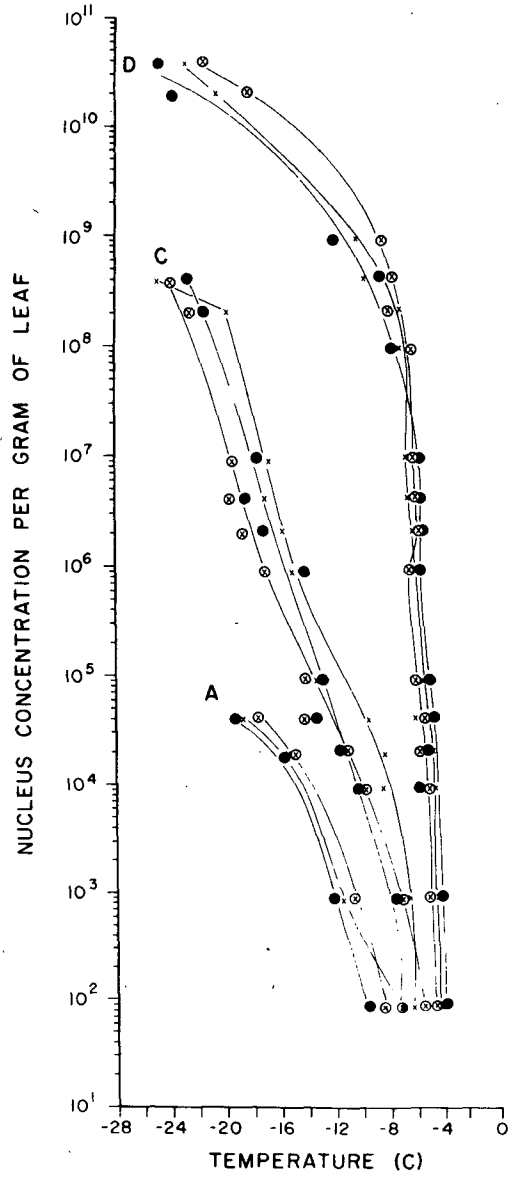

FIG. 1. Freezing nucleus spectra for leaf litters from A-, C- and D-type climate zones. For each zone, the highest, lowest and median spectra are plotted. (Published with permission by *Nature*.)

centimeters to 500 cm^3) was frozen immediately and melted only prior to utilization.

Cloud and sub-cloud water samples were collected from an aircraft by exposing small sterile plastic bags 30 cm beyond the aircraft skin. Both the collection times and sample volumes for the aircraft samples were smaller than for samples collected at the surface. The samples were frozen immediately and melted only at the time of testing.

e. Freezing nucleation measurements

It has been shown by Vali (1971) that the concentrations of suspended freezing nuclei in samples of water can be determined quantitatively by using the drop freezing technique. This technique involves placing equal-sized drops on a thermally controlled surface (cold stage) and monitoring the freezing of the drops as the temperature of the sample is gradually lowered. From the observed freezing temperatures of the drops, nucleus spectra can be constructed.

Samples of leaf litter or of plankton were generally prepared for nucleation measurements by inserting 1 g of the material into 100 g of distilled water. The resulting mixture was stirred, then allowed to stand for 5 min. The sample was then filtered through a coarse paper filter to remove large pieces such as twigs, structural members, insects, etc. A portion of the filtrate was drawn into a sterile syringe which was then used to disperse the sample in the form of drops onto the cold stage. During cooling of the cold-stage, freezing events were detected visually as the drops changed from clear to opaque upon freezing. To characterize the nucleating ability of a sample, the temperatures T_{10} and T_{90} at which 10% and 90% of the drops in a test were frozen, were noted. For the drop sizes used, T_{10} and T_{90} correspond to nucleus concentrations of 10 and 250 cm^{-3}, respectively.

Many samples containing added nucleants were highly active at warm temperatures (−4 and −5°C) causing all drops to freeze within a 2–4°C range. The samples in such cases were diluted 100-fold with distilled water, and if this new solution was still highly active, further 100-fold dilutions were carried out. By taking the nucleus spectrum for each dilution, a composite spectrum could be constructed for the sample over its total freezing range.

f. Isothermal cloud chamber measurements

Samples of well-decayed leaf litters (whole and milled) were tested in a large isothermal cloud chamber (Garvey, 1975). Small amounts of the materials were dispersed by an air blast and ducted into the chamber. Injections of between 5 and 100 mg of leaf material per test were made. Ice crystals produced by the leaf materials were captured on microscope slides and counted visually using procedures described by Garvey (*ibid.*).

3. Biogenic nuclei

a. Leaf-derived nuclei

Early tests with plant leaf materials in the laboratory showed that ice nucleating capacity developed only when the leaves began to decay (Schnell and Vali, 1972). This was found to be the case with leaves from several species of trees, and from widely-separated areas. These nuclei, associated with decayed leaf matter, were given the name leaf-derived nuclei (LDN).

Having found LDN in randomly-selected locations, it became of interest to explore how widespread natural LDN might be. For this purpose samples of well-

decayed leaf litters were collected from 55 dominant tree or grass species across the Northern Hemisphere. One sequence of sampling locations extended across North America, from the Pacific to the Atlantic, and across Europe and northern Asia, from Britain eastward through Siberia to Japan. A second set of samples was collected along a transect from Japan through southeast Asia into western India. A third group came from southern Florida and the Bahama Islands. All the samples were collected between the months of September and December, except the Caribbean samples which were gathered during March and April.

Many of the samples were found to contain freezing nuclei active at -4°C with concentrations reaching 10^9 g^{-1} for nuclei active at -10°C. Other samples contained fewer ice nuclei, by factors of up to 10^5. The abundance of nuclei showed no correlation with species but exhibited a closer similarity among samples from the same geographical location. On further analysis it became apparent that nucleus content is closely related to the climate prevailing at the sample's origin, this factor overriding any possible differences between species of plants.

According to Köppen and Geiger (1954) and Strahler (1965), the earth can be divided into six principal climatic zones (based on average temperature and temperature variation, precipitation amount and physiography). Of the six zones, three have extensive vegetation (A, tropical; C, humid mesothermal; D, microthermal), and the remaining three have lesser amounts of vegetation (B, dry; E, polar; H, undifferentiated highlands). The type of vegatation growing in each climatic zone is generally distinctive for that zone.

Freezing nucleus spectra are presented in Fig. 1 for samples from three climatic zones (A, C, D). Each group contains a minimum of ten samples from at least three continents. For each climatic zone, the highest, lowest and median spectra are plotted. A clear separation between the zones is evident in these data.

Samples of the genus *Poa* were collected within each of the climatic zones A, C and D; samples of the genera *Fagus*, *Oryza*, *Populus*, and others were available from two of the climatic zones. For each of these, the nucleus content of a sample followed the climatic trend and showed no similarity to the other samples of the genus. This fact is demonstrated by the data in Table 1.

There were a few exceptions to the climate-nucleus pattern for samples from mountainous terrain. Also, some of the plants growing under irrigation did not exhibit the same nucleation patterns as nearby plants. Litters collected near boundaries of climate zones occasionally exhibited intermediate nucleation patterns. These samples were omitted from the analyses. Ten samples of leaf litter from moist B-type climate zones (High Plains of North America) were found to be quite similar to those from D climates. This is consistent with the fact that the characteristics of moist B-type climates differ only slightly from dry D-type climates.

TABLE 1. Freezing nucleus contents of samples of leaf litter for the same plant genera from different climate zones. Concentrations are per gram of litter and for activity at -10°C.

Genus	Tropical A-type	Humid mesothermal C-type	Humid microthermal D-type
Oryza	5×10^2	9×10^3	
Poa	3×10^2	9×10^4	$6\times10^8-9\times10^8$
Pinus		4×10^4	$8\times10^8-1\times10^9$
Populus		1×10^4	$9\times10^8-2\times10^9$
Acer		6×10^4	$1\times10^9-2\times10^9$
Fagus		9×10^3	$3\times10^9-5\times10^9$
Quercus		6×10^4	1×10^9

In all, it can be stated that freezing nucleus content in decaying plant litters is governed, with some exceptions, by the prevailing climate. Undoubtedly this comes about because of differences in plant composition and in physical factors which bear upon the progress of decay, and possibly because of differences in microbial populations mediating the decay.

The significance of the presence of freezing nuclei in plant litters for atmospheric processes is clearly dependent on the existence of mechanisms for transferring these materials to the air. No detailed studies of this question have been made to date. On general grounds one can argue that since the litters are located at the air/ground interface some transport to the air is bound to occur. Wind erosion is an obvious possibility but the efficiency of this process would strongly depend on the size, bonding, etc., of the nucleating material. Vaporization and re-condensation is another likely process. The occurrence and magnitude of either of these processes cannot be predicted from present knowledge and experimental determinations also appear quite difficult. For the purpose of demonstrating that transfer of LDN to the air takes place and to obtain a rough measure of the transfer rate, the following experiment was devised.

Freezing nuclei emanating from litter-covered prairie soil (Grover, Colo.), from a weed-covered gravel soil (Laramie, Wyo.), and from aspen and spruce litters (Centennial, Wyo.) were measured during the daytime in the months of August and September. Air above 1 m^2 plots of litter was trapped in an open-bottomed polyethelene "tent," the sides of which were held against the ground such as to allow slight air movement. Air from the tent was drawn out through a single exit port at 25 ℓ min^{-1} and scrubbed with the apparatus described in Section 2b. Samples of the scrubber liquid were taken at intervals throughout an experiment and subsequently measured for their freezing nucleus contents.

From the nucleus concentration in the water, the amount of water used, the scrubber efficiency (determined by separate tests), and from the duration of the experiment, a flux estimate was derived. Control experiments were made by placing the tent over a solid concrete surface.

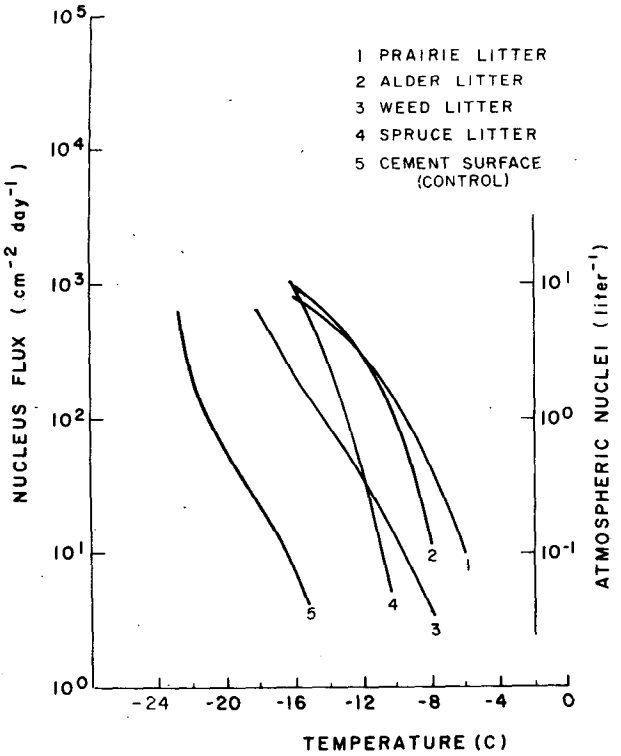

FIG. 2. Flux of nuclei from surface to air for litters of four different vegetation types.

The flux of freezing nuclei from the four litter types was calculated by assuming, for simplicity, that the daytime fluxes for the LDN particles extended over a full 24 h. These data are presented in Fig. 2, showing that from 3 to 300 freezing nuclei active at −10°C were being released per day, per square centimeter of litter surface. The concentrations of atmospheric ice nuclei that would be found in the air above terrains covered by the different litters is shown on the right-hand ordinate of Fig. 2, the calculation being based upon a 10 km ground-to-tropopause mixing depth and a 10-day residence time (Junge, 1963; Weickmann and Pueschel, 1973). These deduced values for nucleus concentrations are somewhat higher than values indicated by direct measurements of atmospheric ice nuclei (Mason, 1971).

To examine the ice-forming ability of leaf materials as realistically as possible, cloud chamber tests were conducted as described in Section 2f. The measured ice-forming power of an aerosol produced from the litter of aspen trees growing in a D-type climate is shown in Fig. 3. The ice-forming power of the milled LDN samples in the cloud chamber tests was slightly less than was indicated by the drop freezing tests. Whole litters, tested in the same state as when collected in nature, exhibited the lowest ice-forming ability. Particle sizes ranged from 5 mm to sub-micron in the whole litter and from 100 μm to sub-micron in the milled material.

While a comprehensive physical and chemical description of LDN has to await further study, some characteristics of LDN have already been established. Filtering LDN suspensions from B- and D-type climates through membrane filters has shown the nucleant particles to be about 0.1 μm in diameter when suspended in water. Chemical tests indicate that the active nucleant material is insoluble and stable in all common organic solvents but begins to lose its nucleating activity upon heating above 60–100°C. The active component of the LDN was found to be 1% or less of the total dry weight of the decaying leaf litter. To date, it has not been possible to identify the molecular structure of LDN particles. Indications are that they consist of potassium and magnesium organic-metallic chelate compounds with a high proportion of carbon, hydrogen and oxygen molecules.

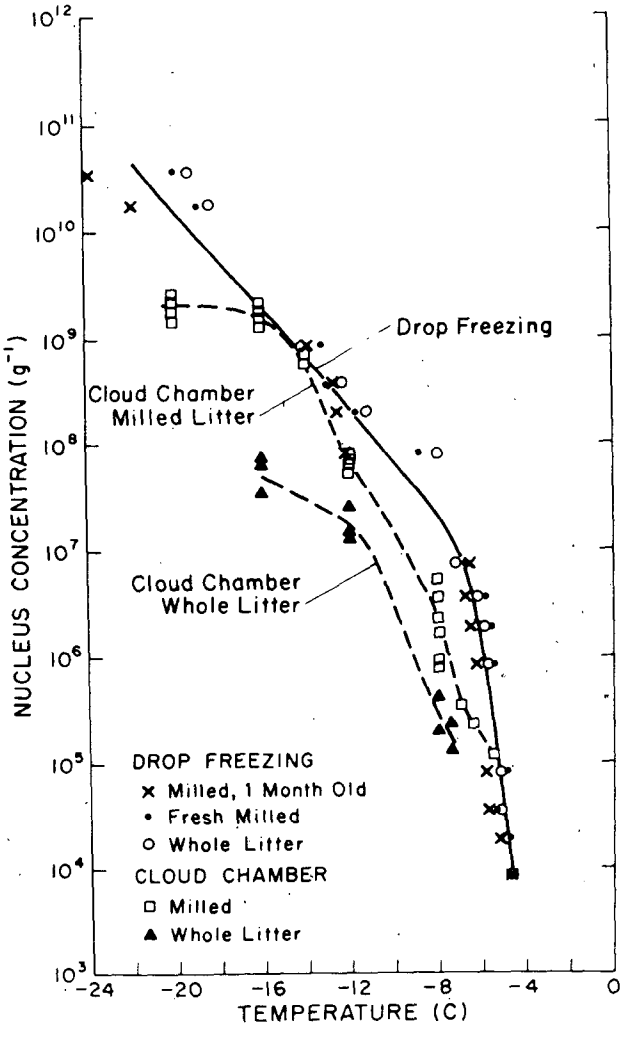

FIG. 3. Comparisons between the ice forming power of a *Populus tremuloides* leaf litter (70-S-14) as tested in water suspension by the drop freezing technique and in aerosol form in a cloud chamber.

b. Ocean-derived nuclei

Samples of surface seawater were collected in the Pacific Ocean off Vancouver, British Columbia (winter) and off Huntington Beach, California (summer); in the Caribbean off Nassau, Bahamas (spring); and in the Atlantic at Bedford Basin, Nova Scotia (spring). The freezing nucleus contents of the samples were determined following the procedures described in Section 2. The results are shown in Fig. 4.

The Bedford Basin samples (curve 4) exhibited considerably greater freezing nucleus concentrations than seawater from the other areas (curves 1, 2 and 3). Bedford Basin had experienced a "bloom period" of phytoplankton growth (i.e., a short-term increase in numbers) just prior to the time of collection of the water sample; the high concentrations of nuclei may have been related to this fact. To pursue this possibility, masses of plankton and associated detritus were sieved from the top 50 cm of the ocean surface in Bedford Basin. Portions of this collected material were tested for nucleation activity within 2 h of collection. The remainder of the sievings were stored in part frozen and in part at ambient temperatures. Microscopic examination showed that approximately 95% (by volume) of the identifiable plankton constituents was phytoplankton and approximately 5% zooplankton. No accurate measurements were made of the amount of the organic debris in the samples, though it appeared that there was more debris in the samples than living component.

A portion of the freshly captured material was prepared for freezing nucleus measurements by reinserting 1 g of the material into 100 g of the original seawater (i.e., seawater shown in curve 4, Fig. 4). The mixture was agitated and allowed to settle for 5 min before filtering through a coarse paper filter. The turbid filtrate was tested for freezing nucleus content and yielded curve 5 on Fig. 4. The difference between curves 4 and 5 (ratio of 10^3 in concentration at -10°C) shows that there are indeed nuclei associated with the plankton matter and suggests that the original activity in the seawater sample was also due to the presence of the plankton matter. These nuclei are referred to as ocean-derived nuclei (ODN).

Seawater has a melting point depression of 2.0°C due to dissolved salts. The inherent nucleating ability of plankton can therefore be better evaluated by suspending the sample in distilled water; 1 g of plankton matter in 100 g of distilled water yielded the spectrum given by curve 6 in Fig. 4. (The concentration here is expressed per unit mass of solid matter.) It may be seen that the Bedford Basin sievings contained some nuclei active at -3.5°C, and 10^7 nuclei per gram active at -10°C.

Filtering the ODN suspensions through membrane filters has shown the ODN to be around 1.0 μm diameter. Activity was destroyed at temperatures exceeding 100°C. Growth from stock cultures of plankton (obtained from the Scripps Institute of Oceanography) has resulted in the successful laboratory cultivation of highly active ODN (first freezings at -2.8°C) and some preliminary results suggest that the ODN are related to living marine bacteria, not unlike the bacteria-derived nuclei (BDN) discussed in Part II.

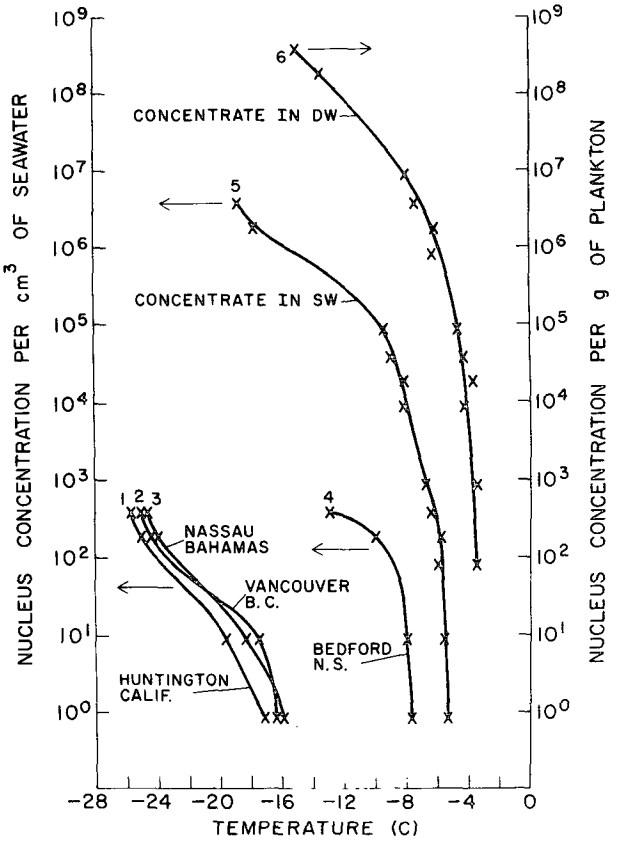

FIG. 4. Freezing nucleus spectra of seawater of low activity (curves 1, 2 and 3) and high activity (curve 4). Activity of plankton concentrate from Bedford Basin is given by curves 5 and 6. (Published with permission by *Tellus*.)

The transfer of materials from the oceans to the atmosphere is well documented. Specifically for organic matter, Blanchard (1964) found that bubbles bursting at a water surface could eject high concentrations of organic material into the atmosphere. Zoebell and Matthews (1936) and Stevenson and Collier (1962) showed that the air above oceans contains numerous micro-organisms indigenous to marine water. Research into the source of organic compounds in snow and rain from New Zealand and Sweden also suggested a marine source for the materials (Wilson, 1959; Neumann *et al.*, 1959).

4. Atmospheric ice nuclei

a. Ice nucleus measurements

1) AUSTRALIA AND THE ARCTIC OCEAN

Ice nucleus measurements for a 3-year period over Australia and the Antarctic Ocean were reported by

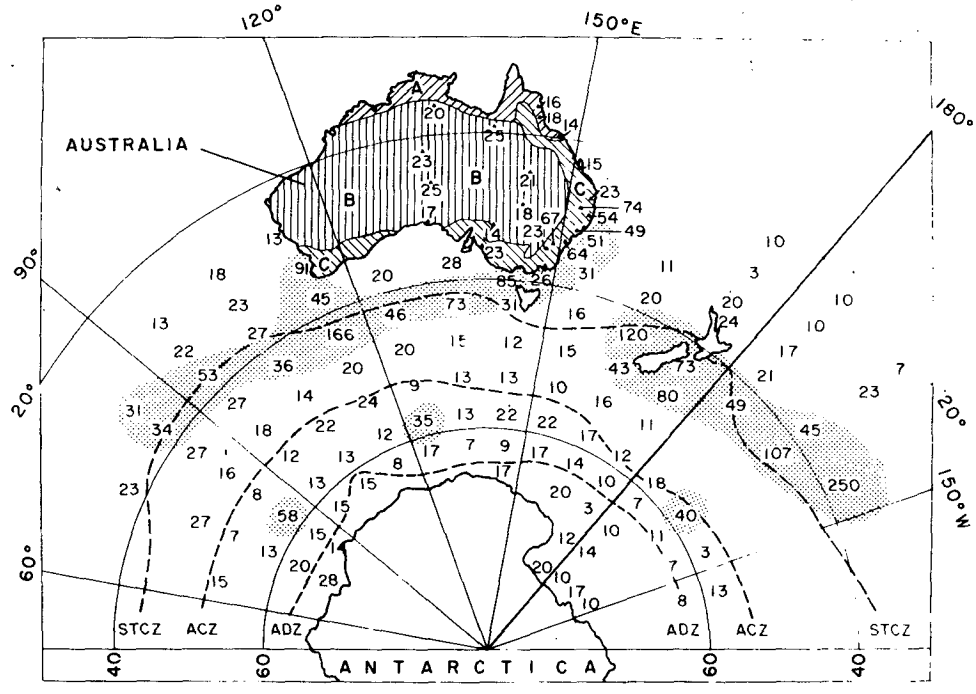

FIG. 5. Three-year averages of atmospheric ice nucleus concentrations over Australia and the Antarctic Ocean plotted on a base map illustrating terrestrial climate zones and marine water mass interfaces. The shaded area encompasses atmospheric ice nucleus concentrations >30 nuclei m^{-3} active at −15°C. Adapted from Bigg (1973).

Bigg (1973). The measurements were made by the membrane filter technique. Bigg noted areas of differing ice nucleus concentrations over both land and water, as well as seasonal variations in nucleus numbers. He suggested terrestrial sources in Africa or South America or extraterrestrial sources as possible explanations for the observed patterns.

The data presented by Bigg were replotted on a map on which outlines of terrestrial climatic zones and marine water mass convergence zones were added (Fig. 5). This shows that on land the lowest atmospheric ice nucleus concentrations are associated with A-type climates, whereas the highest are in C-type climate areas. Dry B-type climates exhibited nuclei concentrations just larger than those from the A zones and considerably less than those from C zones.

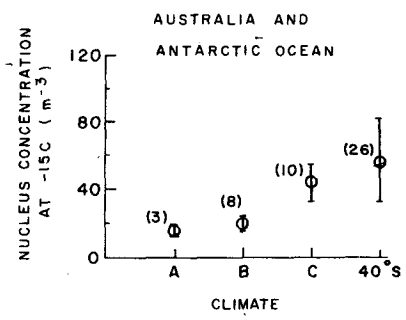

FIG. 6. Average atmospheric ice nucleus concentrations over Australia and the Antarctic Ocean grouped in relation to climate zone on land and the 40°S parallel in the marine environment. The numbers in parentheses indicate the number of stations in each category and the error bars show the magnitude of one standard deviation.

The band of high ice nucleus concentration along the 40°S parallel (shaded area encompasses concentrations >30 nuclei m^{-3} active at −15°C) coincides with the mean position of the subtropical convergence zone (STCZ). This zone represents an area where the meeting of two oceanic water masses results in continual overturning and mixing of the water (Hill, 1963; Fairbridge, 1966). Three smaller pockets of high nucleus concentration lie along the 55–60°S parallel which is near the mean position of the Antarctic convergence zone (ACZ). The relatively high nucleus concentration near the Australian and Antarctic coasts roughly correspond to regions of oceanic upwelling and continental shelf areas (Quom, 1970). Ryther (1963) noted that Antarctic waters are probably the most prolific producers of primary marine plankton in the world, with the output peaking in upwelling zones and to a lesser extent along convergence zones.

To demonstrate the correlation with climate, the ice nucleus measurements shown in Fig. 5 were grouped by climate zones of the Australian continent (A, B and C) and from a 10° band along the 40°S parallel (i.e., STCZ) in the Antarctic Ocean. The averages and ranges of concentrations are shown in Fig. 6.

2) WORLDWIDE MEASUREMENTS

The most extensive set of simultaneous worldwide measurements of atmospheric ice nuclei is that of Bigg and Stevenson (1970). In their study ice nuclei in 300-liter air samples were captured on membrane filters at 44 locations around the world on a daily basis over the months of January, February and March of 1969. The samples were processed at different temperatures; those processed at −15°C are taken as the basis of comparison here because that was the warmest temperature for which the nuclei counts were high enough not to have excessive random variability, and to facilitate comparisons with later data by Bigg (1973).

For our analysis, measurements from D-type climates, which were snowbound at the time of the nucleus measurements, and climate zones with fewer than three sampling sites were not considered. Sites suspected of contamination by AgI generator operations were excluded (Fort Collins, Colorado, and Clermont-Ferrand, France). The remaining sites in A, B and C climate zones numbered 34 and represented about 1000 data days. An additional category (M) was established for stations located less than 150 km away from marine areas which have phytoplankton productivities exceeding 200 g carbon m^{-2} $year^{-1}$. Phytoplankton productivities generally vary between 0 and 400 g carbon m^{-2} $year^{-1}$; the great majority of the oceans produce less than 50–100. The 200 g carbon m^{-2} $year^{-1}$ limit was chosen because it separates the upper 10% in productivities of the earth's oceans (Fairbridge, 1966).

With these criteria Bigg and Stevenson's (1970) data were grouped according to climatic zone, and the mean ice nucleus concentrations for −15°C calculated for each zone by averaging over days and over locations. These results are shown in Fig. 7 by hemisphere and summed for the total earth. Nucleus concentrations are seen to be successively higher for climates A, B, C and M. For climates A, B and C, the same trend was noted in Section 3 for the availability of LDN. It seems that in regions designated by M the high concentrations of ODN and the relative ease of transport of this material to the air could produce high nucleus concentrations.

b. Freezing nucleus concentrations in rainfall

To further pursue the possible connection between biogenic nuclei at surface concentrations and ice nuclei aloft, the regional variation in the freezing nucleus contents of rain samples from convective clouds was examined. Samples were available from a number of places on the North American continent. Collections and analyses were spread over several years but the techniques remained constant throughout. The samples were gathered either at the surface or at about cloud base height, as described in Section 2d. Analysis was by the drop-freezing technique.

A summary of the freezing nucleus contents of rain samples for four regions is shown in Fig. 8. The bands encompass 80% of all samples for a given area, with the number of samples in the groups varying from 37 to 180. The climate zone classification for each area is indicated in the figure; lowest concentrations are in samples from climate A, highest from climates D and B, C being intermediate. This result also is in agreement with the trends noted in Sections 3 and 4a.

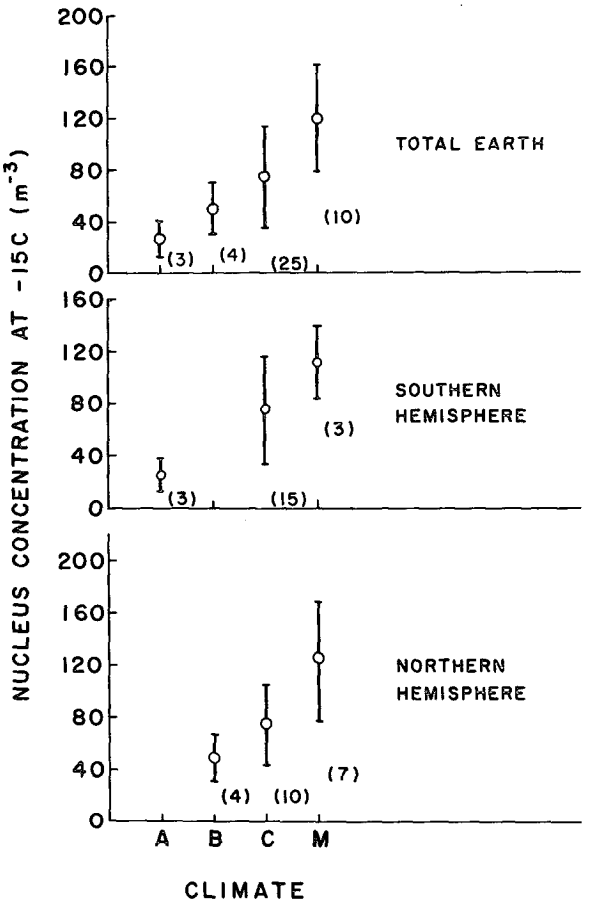

FIG. 7. Average atmospheric ice nucleus concentrations over the total earth grouped in relation to climate zone on land (A, B, C) and proximity to high phytoplankton growth in the marine environment (M). The numbers in parentheses indicate the number of stations in each category and the error bars show the magnitude of one standard deviation. Based on the data of Bigg and Stevenson (1970).

5. Discussion

In Section 3 it was argued that much of the natural ice nuclei found at the earth's surface may be of biogenic origin, and the abundance of these nuclei was found to have a clear correlation with climate. Some tentative values were also given for the flux of nuclei from the surface to the air. In Section 4, data were presented which point to regional variations in the concentrations of atmospheric ice nuclei with the pattern of variation paralleling the availability of nuclei

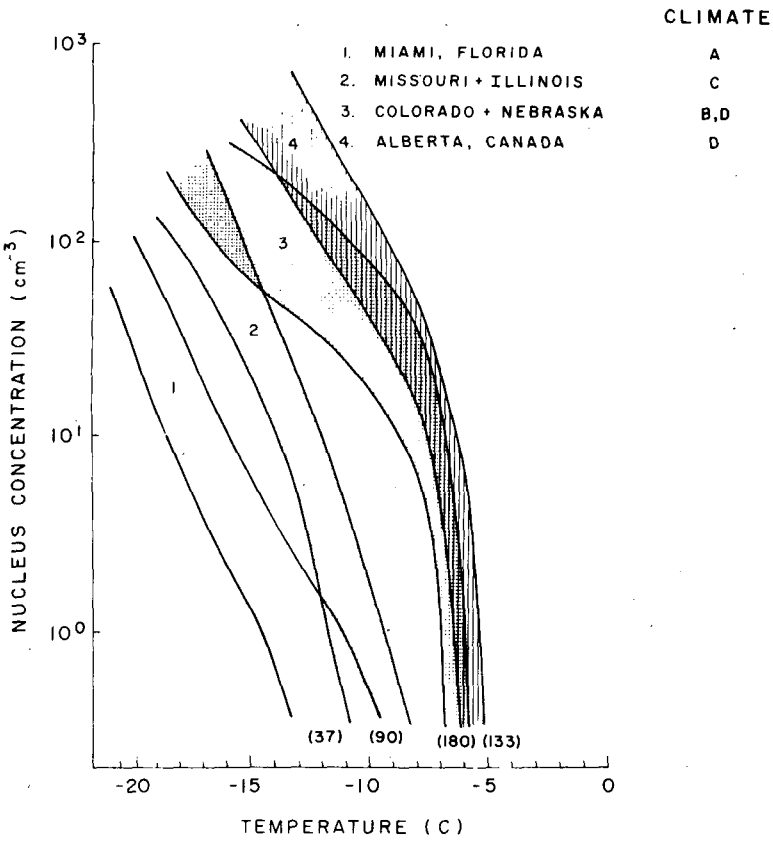

FIG. 8. Freezing nucleus spectra for rain samples collected in four different climate zones in North America. The range is plotted within which 80% of the observed spectra fell for each zone. The numbers in parentheses indicate the number of rainfall samples in each category.

at the surface. The correlation between these two patterns suggests that perhaps a dominant fraction of natural atmospheric ice nuclei originates from biological materials.

Looking at alternative hypotheses for the origin of atmospheric ice nuclei, the most widely held view appears to be that mineral particles provide the majority of nuclei. Detection of clay particles at the centers of snow crystals strongly favors this view. In those studies biogenic materials would not have been detected. Also, clay particles were absent from a fraction of the crystals and direct nucleating ability has not been demonstrated for the detected particles. Furthermore, it is known (Schnitzer and Khan, 1972; Delany and Zenchelsky, 1975) that biogenic materials in soils would be attached to clay particles—from the viewpoint of nucleation the clay may be just acting as an inert carrier. (The size of such an agglomerate could be important in determining its activity in a cloud.) The possibility that the clay particles believed to be the nuclei were in fact attached to already growing crystals could not be completely discounted either. It is also pertinent that regionally the prevalence of airborne mineral dusts would be expected to be greatest in B-type climates (desert, semi-desert and steppe), whereas the nucleus concentration for those regions are relatively low, as shown in Figs. 6 and 7, in agreement with the low organic contents of those soils.

If volcanic sources of nuclei were important, atmospheric nucleus concentrations would probably be highest around the Pacific Rim. Areas in central and eastern North America and Europe would be expected to have lower atmospheric ice nucleus counts. This is not observed. If volcanic materials injected into the stratosphere or extraterrestrial or upper atmospheric materials were important sources of nuclei, it would be difficult to explain the observed correlations with climate and with marine productivity.

If anthropogenic sources were major contributors of atmospheric ice nuclei, one would expect generally high ice nucleus concentrations over the northeastern United States, western Europe and Japan, and localized high counts within the confines of industrial complexes and downwind of industrial cities. Although some localized sources have been documented, these do not appear to be in any way dominating the large-scale patterns. The vast areas of northwestern Canada and Siberia would be expected to be relatively free of ice

nuclei. The measurements of Braham and Spyers-Duran (1974) also speak against this possibility.

An important consideration in discussions of atmospheric ice nuclei sources is the observed vertical distribution of nuclei. While data are sparse, there are some indications that in the troposphere the concentrations of nuclei are greater at higher levels than at the ground (Smith and Heffernan, 1954; Murgatroyd and Garrod, 1957; Telford, 1960; Bigg, 1967). This can only be reconciled with a postulate of surface origin of the nuclei if preactivation of nuclei takes place at cold temperatures (high altitudes), or if nuclei are rapidly deactivated at lower altitudes (perhaps because of coagulation with other aerosols or by absorption of gases). On the other hand, measurements in France and in the United States, using two different techniques, indicated frequent tendencies for nucleus concentrations to decrease rather than increase with altitude. Clearly, better data are needed on the vertical distribution of ice nuclei, although, as pointed out by Mason (1971, pp. 200–202), there are numerous factors involved in explaining the vertical variations of ice nucleus concentrations.

The hypothesis of biogenic nucleus sources should also be compared with the numerous series of point measurements of ice nuclei which have been reported for various geographical locations. Many of those sequences of measurements revealed temporal cycles, short-lived anomalously high counts, or variations with air-mass trajectory. For most such observations, some explanations based on biogenic sources could be constructed, but the lack of data render those explanations too speculative to deserve presentation. Studies of these types specifically testing the hypothesis of biogenic ice-nucleus sources will perhaps be forthcoming in the future.

In all, no claim can be made on the basis of what is presented in this paper that the question of origin of atmospheric ice nuclei has been solved. It is fair to suggest though that the biogenic materials herein discussed show a number of unique features which place them high on the list among possible contributors to atmospheric ice nuclei.

Acknowledgments. This research was materially aided by the cooperation of Dr. T. Platt and B. Irwin of Bedford Institute of Oceanography in collecting plankton samples, by Dr. D. M. Garvey of the Cloud Simulation Laboratory, Colorado State University, in cloud chamber measurements of biogenic nuclei, and by personnel at the Experimental Meteorology Laboratory, Coral Gables, in collection of precipitation samples.

The research was supported, in part, by the National Science Foundation under Grant GI-3255X.

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