

The Composition of Cloud Nuclei

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ABSTRACT

Natural cloud nuclei in both maritime and continental air masses in southeastern Australia (Robertson, N.S.W.) show a high volatility when heated. Few natural nuclei withstand the high temperatures which can be applied to sodium chloride and other sodium salts. Most nuclei are therefore something other than sodium chloride or sea salt—probably ammonium sulfate. The concentration of non-volatile nuclei which could be sea salt rarely exceeded 10 cm^{-3} .

1. Introduction

The composition of natural cloud condensation nuclei is of some interest, particularly as a possible indication of the sources of these nuclei. Observations to date suggest that although bursting bubbles (at the ocean surface) and urban-industrial pollution (at the land surface) are sources of cloud nuclei, the major source is neither of these. Near the surface, nucleus counts over land are on the average about ten times more numerous than over the ocean, but they decrease more rapidly with height; and since they have been found to be at least as numerous over Africa and Australia as over North America and Europe, a continental source, other than man-made pollution, seems to be required. The observed numbers of nuclei over land and their probable residence time imply a mean production rate of the order of from 10 to 100 nuclei per square centimeter of land surface per second. If they are produced in the air rather than at the surface a production rate of 10^{-4} – $10^{-3}\text{ cm}^{-3}\text{ sec}^{-1}$ seems to be necessary.

Of the soluble salts which have been found in the atmosphere, sodium chloride and ammonium sulfate greatly outweigh the rest both in amount and in ubiquity. Junge (1963) has concluded that sodium chloride (probably as sea salt) is the major component in the "giant" particle size range above $1\text{ }\mu$ diameter, with ammonium sulfate the major component in "large" ($0.1\text{ }\mu < d < 1\text{ }\mu$) particles. Although soluble particles in the latter range of sizes will certainly act as cloud nuclei, measurements of diffusion coefficients and direct visual observations of natural aerosols in intense illumination both suggest that most cloud nuclei are less than $0.1\text{ }\mu$ radius, tending to fall in the 0.01 – $0.1\text{ }\mu$ range rather than in Junge's "large particle" category. They therefore constitute only a rather small proportion of the aerosol mass below $1\text{ }\mu$ radius.

2. Preliminary considerations

Cloud nuclei are only a few hundredths of a micron in radius, or about 10^{-16} gm in mass. Direct analysis

would therefore be extremely difficult. The writer has carried out experiments (unpublished) to separate the cloud nucleus material from the atmospheric aerosol as a whole by allowing condensation to take place at low, cloud-like supersaturations and collecting the droplets formed. The experiments had to be continued over periods of the order of months to achieve even marginally detectable amounts of material, and the condensed droplets were susceptible to contamination during condensation and after collection by absorption of, or reaction with, gaseous atmospheric contaminants. The results showed a predominance of sulfur, with large relative amounts of iron, nickel and sodium, but they could not be regarded as decisive in view of these questions of the contamination.

In spite of its lack of specific analytical power, an experiment in which some physico-chemical property is measured, without condensation upon or capture of the nucleus, has the virtue of being free from difficulties introduced by possible contamination. In the experiments discussed here the nuclei were heated during their passage through a hot tube to temperatures high enough to evaporate many compounds; in this way a curve of relative number vs tube temperature or heater voltage was obtained and could be compared with curves derived by using artificial aerosols of known composition. Although composition obviously cannot be obtained uniquely from such experiments, the range of possible composition can be narrowed down.

3. Experimental procedure

The heater was a silica tube 1 m long and 1 cm in diameter, heated electrically by a winding which extended over a 55-cm section of the tube. The usual flow rate was 25 ml sec^{-1} , which meant that a particle on the axis spent ~ 0.75 sec in the heated section of the tube.

Artificial nuclei, similar in size to natural cloud nuclei and produced by bubbling particle-free air

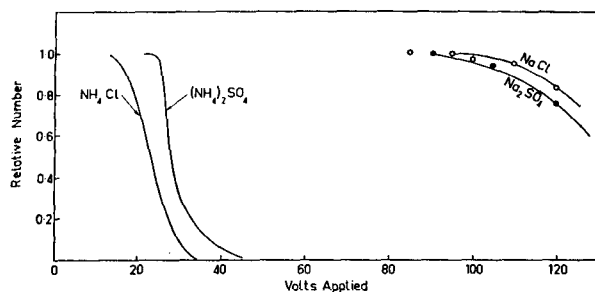


FIG. 1. Behavior of artificially produced nuclei with increasing temperature.

through a solution of the compound in question, gave the data¹ shown in Fig. 1. These nuclei were similar in size to natural cloud nuclei.

The nuclei were counted photographically in a thermal diffusion cloud chamber at 0.75% supersaturation. Particles $\leq 1.5 \times 10^{-6}$ cm radius are incapable of nucleation under these conditions so that the majority of the Aitken nuclei were not observed. The fact that boiling-off curves such as those in Figs. 1 and 2 can be obtained shows that when the heated air cools back to room temperature any recondensation of the evaporated material which takes place occurs either on the walls or into particles too small to activate condensation in the diffusion cloud chamber.²

Fig. 1 shows that the sodium salts tested gave nuclei which had to be heated much more than the ammonium salts to bring about their evaporation.

4. Theory of the evaporation mechanism

Theoretically there is little difference between the evaporation of solid particles and the evaporation of water droplets. It should be possible to calculate boiling-off curves for particles of any material provided the vapor pressure, surface free energy, accommodation coefficient and diffusion coefficient are known for the conditions of the experiment. Such data are not available for most substances, but in the case of ammonium chloride and sodium chloride, the various parameters, except for the accommodation coefficient, are known or can be estimated within reasonable limits; application of Fuchs' (1934) equation for the evaporation of spherical particles for various assumed values of the accommodation coefficient, gave excellent agreement with experiment for an accommodation coefficient of 10^{-2} . The presumption that the reduction in particle number during passage through a heated tube is due to evaporation of the particles is therefore supported by the comparison of experimental results with theory.

¹The abscissa "Volts Applied" in Figs. 1-3 refers to the voltage applied to the heater winding around the silica tube.

²Dinger (personal communication) has found an increase in Aitken count when larger particles are boiled off; it is therefore probable that some of the evaporated material of the nuclei originally present recondenses back into the aerosol, but in a smaller size range.

5. Results

a. Experiments on volatilization

Results in the Northern Hemisphere (Twomey, 1968), derived from measurements in the Washington-Baltimore area, showed a consistent pattern of behavior, with the majority of the nuclei evaporating at quite low temperatures and very few natural nuclei surviving to the higher temperatures which artificial sodium chloride nuclei, for instance, could withstand. The observations did not, however, include any clear-cut cases of unmodified maritime air, and were obtained in an area where a fairly high level of general pollution prevails. A further series of measurements have now been made in southeastern Australia, at a site (Robertson, N.S.W.) which is subject to appreciable pollution from one wind quadrant only—east to north—wherein pollution from the industrial Wollongong-Port Kembla region (15-20 mi away) and the Sydney metropolitan area (60 mi away) can reach the site. The presence of such pollution is easy to recognize at the sampling site.

Median data for boiling-off cloud nuclei in polar maritime, tropical maritime and continental air masses are shown in Fig. 2. Each curve is similar to the curves given elsewhere for the northeastern United States and the curves given by artificial ammonium sulfate (or chloride) nuclei. The data for polar maritime air are particularly noteworthy because these represent an exceptionally clean maritime air mass with a very long trajectory over the Southern Ocean (probably similar to the GHOST balloon trajectories). There was no tendency for a greater fraction of non-volatile nuclei to occur in this kind of air mass.

During the course of the observations, there were occasions when the sampling site was visibly contaminated by local fires (within a distance of ~ 5 mi); on other occasions widespread but more distant (> 100 mi away) bush fires raised the general pollution level and gave high counts of cloud nuclei. The aerosol from the local fires was found to contain nuclei which boiled off at a heater voltage well above that needed to evaporate ammonium sulfate (but less than that needed to evaporate sodium chloride particles). On the other hand, the particles from the more distant fires behaved in the same manner as ammonium sulfate or normal natural cloud nuclei. This result implies either that the two kinds of fires were fundamentally different or that particles were still being formed within the polluted air as it travelled away from the fires, these particles differing in composition from those produced directly by the fires or in their immediate vicinity. It is not at all unreasonable to expect that less volatile compounds would, in fact, condense out first; on the other hand, even the more volatile compounds would be expected to condense out in a very short time unless they, or the materials from which they were being produced, were being formed slowly. This is quite likely if slow photochemical reactions are involved.

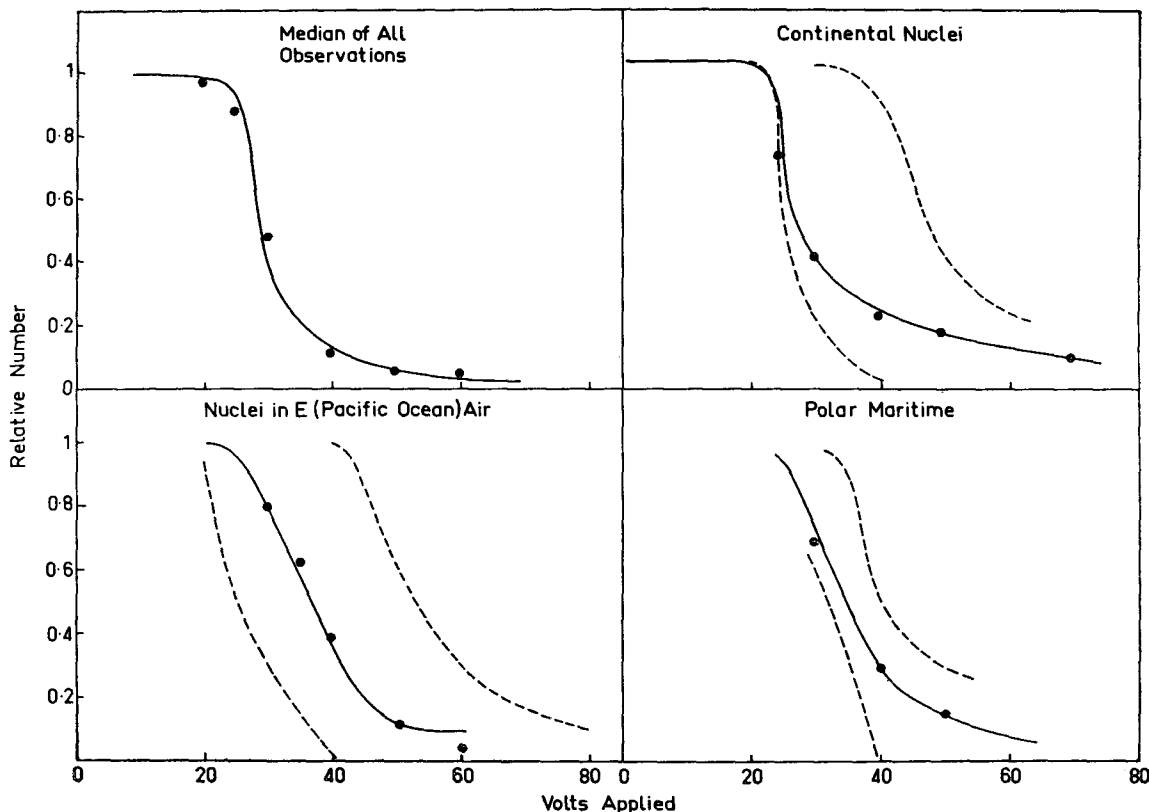


FIG. 2. Behavior of natural cloud nuclei in various air masses.

If the cloud nuclei produced by distant fires were ammonium sulfate, or a similar compound, formed within the polluted air mass, it seems plausible that the nuclei in unpolluted air mainly originated in a similar way.

b. Experiments on nuclei production

Simple experiments were carried out to assess nucleus production at land and sea surfaces and in the air.

1) SEA SURFACE. Bubbling filtered air through either NaCl solutions or natural sea water produced nuclei effective at very low supersaturation, with no or very few additional Aitken-type particles ($<0.01 \mu$, active

only at higher supersaturations). About 100 nuclei were found to be produced by each bubble. The nuclei produced by bubbling clean air through sea water behaved exactly the same as nuclei from sodium chloride solutions with respect to vaporization, requiring a high temperature for their removal.

2) LAND SURFACE. A collection of soluble soil material was obtained by washing the solubles from a sample of local soil. Bubbling clear air through this solution produced nuclei which were similar in behavior to NaCl or sea salt. This result suggested that a mere removal of soluble salts from the surface or emission from the surface, such as was described by Twomey (1960), would give a nucleus different in composition to most natural nuclei. It is possible that a different result might obtain with a soil sample from another location, and it is also possible that a different composition prevails right at the surface, but neither appears very probable.

Experiments were also carried out in which clean air in a bell jar inverted over the soil surface was periodically examined. Occasional nuclei were observed, but the estimated rate per square centimeter of surface rarely exceeded the observable limit of about $0.5 \text{ cm}^{-2} \text{ sec}^{-1}$ and was generally well below this. (The nucleus concentrations were too sparse to permit any boiling-off tests to be done.) This rate of production is totally

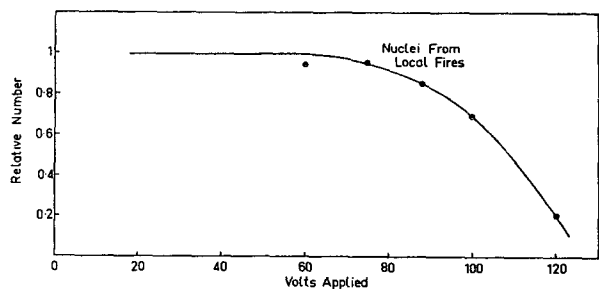


FIG. 3. Behavior of nuclei in air polluted by local fires.

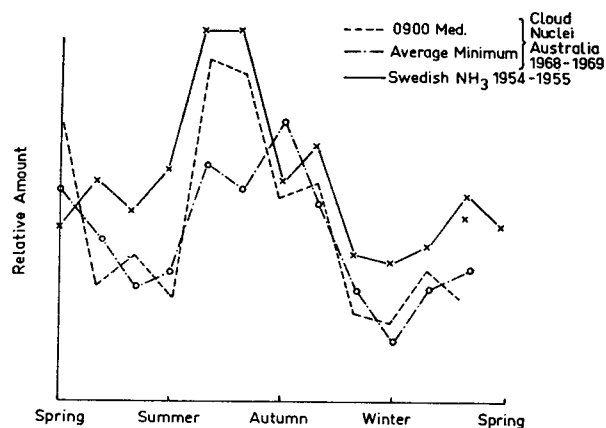


FIG. 4. Comparison of seasonal pattern of nucleus variations with seasonal ammonia variation obtained by Egner and Eriksson (1955).

inadequate to explain the observed nucleus concentrations found in the atmosphere, since even in a 1-km atmospheric column it would add no more than $0.5 \text{ cm}^{-3} \text{ day}^{-1}$ to the average columnar nucleus population.

3) PRODUCTION WITHIN THE AIR. Similar bell jar experiments were made with and without irradiation by a mercury lamp within the bell jar. Production never exceeded the limit of detection ($\sim 0.01 \text{ cm}^{-3} \text{ sec}^{-1}$). This minimum rate, however, would still give $1000 \text{ cm}^{-3} \text{ day}^{-1}$, so these experiments did *not* rule out airborne production of nuclei as a possible major source.

4) URBAN-INDUSTRIAL POLLUTION. The sampling site was subject to pollution in a well-defined range of wind direction. The increase in concentration produced by the arrival of polluted air was on the average some $1500\text{--}2000 \text{ cm}^{-3}$. For average conditions this gave an estimated production rate of $10^{13}\text{--}10^{14}$ cloud nuclei per second by the area concerned, the Wollongong-Port Kembla region. This region is highly industrialized and accounts for a sizable fraction of Australia's iron and steel production; nevertheless, the observed nucleus production is very small compared with the estimated nucleus production by the Australian continent, which is of the order of 10^{19} sec^{-1} . The Wollongong-Port Kembla region has a population of $\sim 200,000$, produces close to 4 million tons of raw steel annually, and consumes some 2.5 million tons of fuel annually. Extrapolation to the whole earth in proportion to steel production would give a global urban-industrial production of nuclei of $\sim 10^{16} \text{ sec}^{-1}$. Extrapolation on a population basis would give a world figure of only about 10^{18} sec^{-1} which is far below the estimated world production of nuclei [Twomey and Wojciechowski (1969), for example, estimate 10^{21} sec^{-1}].

These figures suggest that direct particulate pollution from urban-industrial regions is not, as yet, a major source of cloud nuclei. However, pollution may also

play a role in adding gases to the atmosphere which subsequently react and produce particulates.

6. Discussion

It seems quite certain that most cloud nuclei, in both Northern and Southern Hemispheres and in both maritime and continental air, are composed of a relatively volatile material similar to ammonium sulfate and certainly not sodium chloride or sea salt. Sea-salt nuclei, presumably produced by bubbles bursting at a sea-water surface, have been found, but even in maritime air they were usually far fewer than the more volatile nuclei. Dinger *et al.* (1970) found that sea-salt cloud nuclei were a minor proportion over the North Atlantic and (at least in a subsiding air mass) were confined to the lowest couple of kilometers. A minor non-volatile fraction which is probably sodium chloride or sea salt was found in our experiments, but the concentrations rarely exceeded a few per cubic centimeter and very rarely reached a few tens per cubic centimeter.

No evidence was found that the increased numbers over land were occasioned by nuclei produced directly at the surface. The mechanism proposed by Twomey (1960) does not seem to be sufficiently productive to account for the concentrations which actually occur. However, the vertical decrease in nucleus numbers over land does suggest that the surface plays a big part in the main production process. The most obvious indirect role would be through the release of a gaseous material which subsequently reacts to produce solid materials. If the nuclei are ammonium sulfate produced by reactions between gaseous ammonia and gaseous sulfur compounds, it is possible that ammonia is what is contributed by the land surface toward the production of cloud nuclei. Junge (1963) states that the soil surface is a major source of atmospheric ammonia, the ocean a minor sink, and pollution not a sizable source except locally; a similar summing-up applies to cloud nuclei.

The similarity in composition of the majority of nuclei in both maritime and continental air masses suggests strongly that the same dominant mechanism of production is at work in both instances. A slow reaction between gaseous components of which one (at least) originates at the land surface would accord with the main features of cloud nucleus distribution and composition. It is interesting that some similarity exists between the observed annual variation in cloud nuclei at Robertson, N.S.W., in 1968-69 and the annual variation of atmospheric ammonia for the Swedish network during 1954-55; this is shown in Fig. 4, where Swedish data were displaced six months to allow for the hemisphere difference. The scales are purely relative and the curve cannot be considered as anything more than suggestive. Concurrent measurements of nuclei and atmospheric composition would be needed to establish whether any real association existed.

It might be noted that at elevated temperatures ammonium sulfate is almost as volatile as ammonium

chloride. If the same is true at atmospheric temperatures, then the Fuchs evaporation equation gives a short lifetime (of the order of hours) for ammonium sulfate nuclei in an atmosphere unsaturated with respect to the vapor, so that the nucleus concentration could diminish through evaporation. In the complex gas-solid mixture existing in the atmosphere such a reduction in vapor concentration need not imply a reduction in overall concentrations since it might also be brought about by a displacement of the equilibrium of one or more of the several chemical reactions involved.

7. Conclusions

1) Most cloud nuclei in the atmosphere are not sea salt or sodium chloride, even in maritime air with a long residence over the ocean. It seems likely that most nuclei have a similar composition (at least where the soluble part of the nucleus is concerned) whether over land or over the ocean; our experiments are consistent with nuclei composed of ammonium sulfate.

2) A small and highly non-volatile fraction, probably sodium chloride or sea salt, is also found, but in concentrations rarely exceeding a few to a few tens per cubic centimeter.

3) Continental nuclei do not in the main originate directly at the surface, although the observed vertical decrease in numbers does suggest that the surface plays a part in the process.

4) The similarity in composition of the majority of both marine and continental nuclei suggests that a single major source is at work in both air masses and that the large differences between the two kinds of air mass are not due to an additional mechanism operating over land.

5) The role of land masses does not seem to be primarily the direct release or emission of nuclei but rather the release or emission of a gaseous component which takes part in the production of the nuclei in the atmosphere. Ammonia may be this gaseous component.

6) The similarity in number and probable composition of nuclei in northeastern United States and southeastern Australia discounts the possibility that urban-industrial pollution plays a large part in the formation of these particles. This conclusion is supported by extrapolating observed nucleus production from urban-industrial pollution to a global figure and comparing the result with estimates of global nucleus production.

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