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The aerosol in a boreal forest in spring

By E. K. BIGG, *12 Wills Avenue, Castle Hill, New South Wales 2154, Australia*

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ABSTRACT

Particles >30 nm diameter collected in a forest in Finland from 22 April–4 May 1998 and from 23 March–16 April 1999 were examined by transmission electron microscopy. The 1st period had no nucleation events, the second had many and differences in particle properties are described. Particles predominantly 100–200 nm in diameter and having a large organic content were found to accumulate in an enclosure above a snow surface in the forest. The explanation given is that on sunny days water from melting snow penetrated the soil and leaf litter beneath the snow, displacing gases produced by decomposition of organic material. It is assumed that the bursting of bubbles produced at the soil–snow interface by the escaping gases led to the production of the particles in the enclosure. Soil pit data at the site showed that on sunny days water commenced to penetrate to at least 29 cm soon after sunrise and reached a maximum in early afternoon. Particles similar to those found in the enclosure were present in the free atmosphere on days with nucleation events. Data from other observers showed that compounds that might be expected to arise from soil emissions were all present in greater concentrations on days with nucleation events than on days without. It is suggested that the material for production of condensable vapours leading to the nucleation and growth of particles was contained either in the escaping gases or in the aqueous material initially surrounding the particles produced by bubble bursting. The hypothesis has the advantage of explaining the very sharp maximum found in spring as the winter snow melts.

1. Introduction

Mäkelä et al (1997) and Kulmala et al. (1998) have described nucleation events observed in a boreal forest at Hyytiälä, Finland, (latitude 61.85°N, longitude 24.3°E). They found a sharp maximum in the frequency of such events in early spring with a secondary smaller maximum in autumn. The newly formed particles appeared on average about 4 h after sunrise and a decrease in particle concentration was observed about an hour before to an hour after the onset of nucleation on two-thirds of the occasions. They supposed that morning sunlight drives photochemistry that produces condensable vapours while vertical mixing generated suitable thermodynamic conditions for nucleation to occur. The growth of the particles was too rapid to be explained by deposition of sulfuric acid and it was speculated by Kulmala et al. (1998) that organic acids were responsible. Campaigns ("Biofor") to seek the nature of trace gases that might have led to particle production and growth, the associated physical conditions and the chemistry of the aerosols were mounted in 1998 and 1999. There are two likely sources of organic compounds in a forest. One is the terpenes emitted by pine trees and other vegetation and this was intensively studied during the Biofor campaigns. Janson et al. (2001) have shown that the concentration of oxidation products of terpenes should have produced sufficient condensable vapours to account for particle growth. Their rate of formation was expected to be greatest at night. The second possible source of material is decomposition products of organic material in the

* Corresponding author.
e-mail: keith@hotkey.net.au

soil or leaf litter. Mäkelä et al. (1997) foreshadowed this source by suggesting that soil micro-organisms may have been involved in the production of organic compounds in the air that led to particle nucleation or growth. Swift et al. (1979) have discussed the processes of decomposition in a boreal forest. Polysaccharides, proteins and lipids are the main sources of energy and are broken down by enzymes into smaller units such as mono- or di-saccharides, amino acids, dipeptides etc. A very wide variety of compounds including carbon dioxide, ammonia, amines, and many carboxylic and dicarboxylic acids can result from further breakdowns. Because of the large growth experienced by particles following nucleation events, those compounds taking part in growth should have higher concentrations on days on which nucleation of new particles occurred ("event days") than on non-event days, whatever their source may have been. Mäkelä et al. (this issue) list the ions detected in collections of aerosols made by impactors on event and non-event days. The greatest difference in abundance between event and non-event days occurred for the dimethylamine ion — it was almost absent on non-event days and in concentrations comparable to those of the ammonium ion on event days. Other ions that were more prevalent on event days (but not to the same extent as dimethylamine) were ammonium, sulfate and a number of carboxylic and dicarboxylic acid ions. Janson et al. (this issue) also found ammonia and sulphur dioxide (SO_2) to be present in higher concentrations on event days. With the exception of SO_2, each of these ions could have been produced from degradation of organic material in the soil.

This paper will describe distinctive particles, mostly larger than 100 nm, emitted into an enclosure above a snow surface and show that some similar particles were present in the outside aerosol. It will then discuss a possible process leading to their production that suggests the sources of daytime particle formation and growth in the atmosphere.

2. Methods

Particles were collected directly onto transmission electron microscope grids by electrostatic or thermal precipitation and by impaction. The first two methods required 8- to 12-h samples in order to obtain a sufficient particle density on the grids for easy examination and did not collect a detectable number of particles smaller than 30 nm. The impactor, with 50% collection efficiency at about 150 nm collected a large number of particles in only a few minutes.

Artificial "shadows" were imposed on the collected specimens before examination in the electron microscope in order to improve the contrast between small and almost electron-transparent particles and the substrate. This was achieved in a vacuum by firing a beam of metal atoms (or silicon monoxide) on to the specimen at an angle of 26.6° so that the metal-free shadows were twice as long as a particle's height. This allowed the volume of the dry particle and hence the diameter of a sphere of equivalent volume to be deduced and the outline remained even if the particle was volatile under the heating of the electron beam during examination. Also, when a partly soluble specimen was floated on water, the original outlines of the particle and its shadow were preserved, so that the proportion of insoluble material could be estimated.

Since production and growth of particles in a forest suggests that organic compounds could be involved, a simple but relevant test was to subject them to the saturated vapour of various organic solvents. If soluble in a particular solvent, exposure to its vapour caused the particles to swell and extend beyond their original position. This usually lifted the shadowing material or left residues, sometimes crystalline, when the solvent evaporated. A further test for organic material (particularly that with unsaturated double bonds) was to subject the specimens to the vapour of osmium tetroxide. Reaction sites were revealed by the very electron-opaque osmium deposited.

In Section 1, it was noted that a soil source of nucleating material had been suggested and that amino acids were among the many products of breakdown of material in leaf litter. For this reason a test for the presence of amino acids was developed for the present study. Doherty et al. (1940) have described the use of aromatic benzene sulfonic acids to detect amino acids, very water-insoluble compounds being formed by reaction in solution. The acid used here, 8-hydroxy-5,7dinitro-2-naphthalene sulfonic acid (sodium salt) was one those authors found to produce the least soluble

compounds with many amino acids. It is also known by the simpler names of flavianic acid or naphthol yellow. A "Millipore" filter was placed on a porous "nutrient pad" soaked in a weak solution of the reagent. The electron microscope grids were then laid on the filter with the particles uppermost. Water and ions penetrated the butvar/carbon substrate and reacted with any amino acids, depositing insoluble compounds, while soluble compounds leached away. The specimen was then transferred after about 6 h to a second filter on a nutrient pad wet with distilled water in order to remove the reagent and any remaining soluble material. A similar procedure was used to detect sulfates, by replacing the flavianic acid with a saturated barium fluoride solution. Sulfates formed the very insoluble barium sulfate.

The osmium tetroxide and flavianic tests were not introduced until the 1999 campaign, the 1998 results having suggested that they might be important.

Throughout this paper, all particle sizes are given as diameter of a sphere of the same volume and refer to the size after exposure to a vacuum.

In the electron micrographs shown, electron-opaque regions appear black. Electron-transparent regions, including the shadows, appear white. At high magnification the shadowing material can be seen to have coagulated into particles of a few nanometres diameter, giving a mottled or spotty background.

3. Release of organic compounds and aerosol from leaf litter and soil

During winter and early spring, the forest at Hyytiälä was covered with deep snow. Soil pit records at the surface, 4 cm, 16 cm and 29 cm depth were available for the site during the 1999 spring campaign. The nocturnal temperatures in the top 29 cm of soil were warmer than 0°C in spite of colder air temperatures and the overlying snow, presumably because of heat released by decomposition processes. On sunny days it was observed that as air temperatures increased, soil temperatures in each of the strata down to 29 cm fell, reaching a minimum at about 13h30m on average. Fig. 1 shows the mean curves of temperature in the air and at the soil surface for a period of 9 successive days in April 1999, 8 of which were sunny and had conspicuous particle production and growth during late morning and afternoon.

The obvious interpretation of the soil temperature curve is that water from melting snow at a temperature of 0°C had penetrated the leaf litter and lowered the temperature. It penetrated at least to 29 cm. In doing so, it would collect soluble material from the soil and would displace pockets of trapped gases produced by microbial decomposition of organic material. Some bubbling caused by the escaping gases would be expected in the process. One of the notable characteristics of the forest was the amount of surfactants in the soil. Every small waterfall produced rafts of bubbles and a mound of extremely tough foam. It is therefore suggested that bubbles stabilized by the surfactant material and including in their films other soluble compounds were formed at the soil–snow interface by the released gases. As the bubbles burst some of the bubble film material escaped through the interstices of the snow producing small mainly liquid drops.

If the above assumptions are correct, a container placed over a sample of ground should collect a certain number of particles from bubble bursting. To test this a 100 L plastic bucket was upended and its rim embedded to soil level in loose uncompacted snow about 30 cm deep over level ground between pine trees. Inlet and outlet tubes were led into it from below, snow piled to 60 cm around the outside and compressed to reduce contact with the outside air. For 24 h, the internal air was recirculated through a "Fluoropor" 2 μm filter to remove the natural aerosol. Sampling then began with the thermal precipitator at an airflow of $0.2\ cm^{-3}\ s^{-1}$, the specimens being changed every fourth day. The bucket was not moved until the end of the experiment but the surrounding snow was kept at a depth of 60 cm.

The number of particles collected from within the bucket (Section 2) was surprisingly large, exceeding the average concentration obtained by an identical thermal precipitator sampling the outside air, even on the first sample where the initial concentration in the bucket was zero. It therefore seems certain that most of the particles originated within the container and had not diffused in from the outside air.

It was not possible to estimate the rate of production of the particles from the soil. Losses of particles in the container by sedimentation

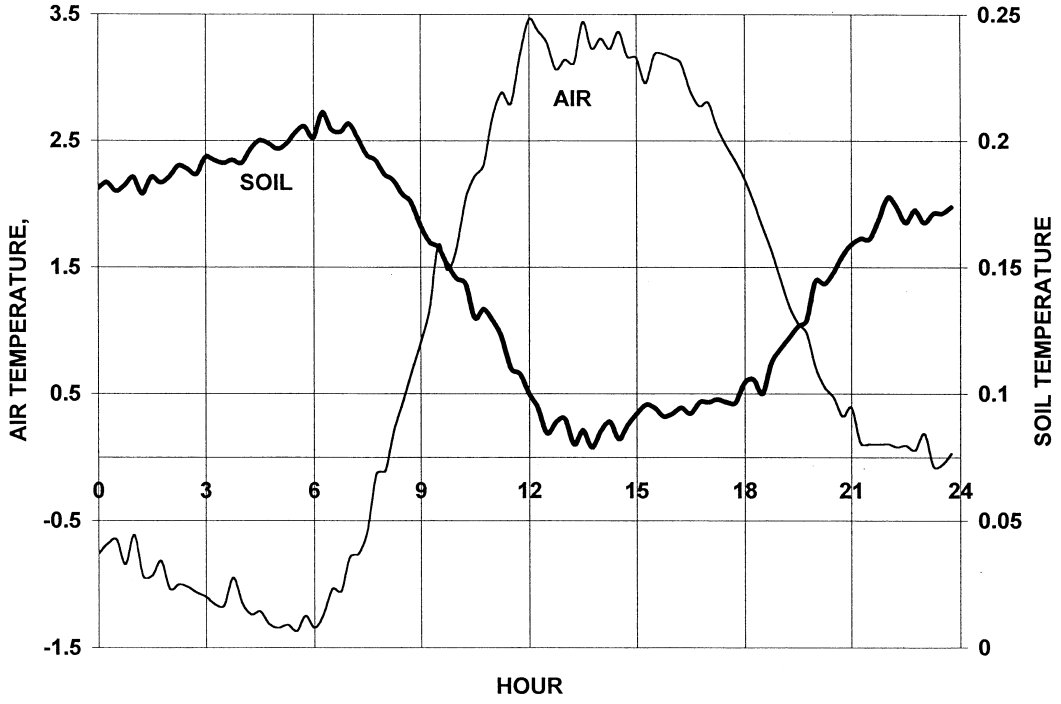

Fig. 1. Mean soil temperature at the surface, 5–13 April, 1999 as a function of time.

would have been altered by convection during intermittent sunshine, losses by diffusion to the walls could have been enhanced by electrostatic charges on the plastic container and losses by thermal diffusion could have varied throughout the day.

Particles after having been subjected to a vacuum were predominantly in the size range 100–200 nm although the thermal precipitator favored collection of smaller particles. Unlike the wide variety of particles in the outside air, all were quite similar. They were solid and most were roughly spherical as in the example of Fig. 2A although a few were irregular aggregates of crystalline particles of 30–50 nm, similar to that shown in Fig. 4A. The edges of the particle of Fig. 2A suggest that it contained many much smaller particles. Particles like this were almost completely dissolved by decane vapour and as the decane evaporated very distinctive crystals formed. Fig. 2B shows an example that contains the three most common crystalline forms. Another property of the particles was that most reacted in varying degrees with flavianic acid, indicating the presence of amino acids. In Fig. 2C, the shadow shows the original outline of the particle which appears to have been composed of two touching spheres. The wider electron-opaque ring represents the precipitate formed by the reaction while the central very electron-opaque area is either a reaction product or a water-insoluble component of the original particle (or both). When an electron microscope grid with its specimens uppermost was floated on distilled water, particles such as that of Fig. 2A usually left a residue of small rather than large components after the soluble components were leached out.

Particles derived from bubble films when bubbles burst on sea water have been found to retain a liquid appearance when captured, even after having been subjected to a vacuum (Bigg and Leck, 2001). In sea water, high molecular weight compounds such as soluble proteins are likely to be preferentially scavenged by bubbles (Gershey, 1983) and evidently do not readily part with their water. In the present experiments, par-

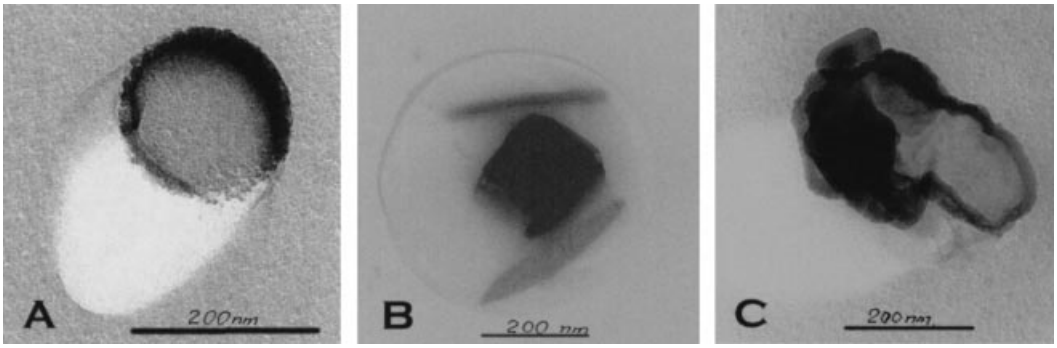

Fig. 2. Particles emitted from soil in spring 1999 and collected in an enclosure. (A) Typical appearance. (B) After exposure to decane vapour. Note the crystals formed. (C) Reaction of particle with aqueous solution of flavianic acid, revealing the presence of amino acids.

ticles within the enclosure did not have this liquid nature after having been exposed to a vacuum. If derived from bubble films, there must have originally been a liquid component but it had evaporated before examination.

The conclusions from this experiment were that particles were being emitted from the soil and some escaped through the loose snow. (They were far too large to have grown in situ.). The particles were largely organic and contained some amino acids. The implications will be discussed in Section 6.

4. Collections of particles made during late spring in the absence of nucleating events

During the period 22 April–4 May 1998, there were no clear nucleation events. Snow cover was initially thin and disappeared after the first few days with the advent of warm weather. Particles collected in the relatively unpolluted first five days were unlike those usually encountered in clean continental air masses in that a large proportion resembled the particle shown in Fig. 3A with a solid centre surrounded by a volatile liquid. Particles of a type not previously encountered elsewhere appeared from their size (50–100 nm), geometrical patterns on their surface and insolubility in water to be viruses. While only forming $<1\%$ of the particles in their size range, they were very conspicuous. Most were surrounded by a liquid that evaporated when heated in the electron beam. An example is shown in Fig. 3B.

After 27 April, a warm southerly airstream brought more polluted conditions. Very liquid particles dominated even when the relative humidity was low and they usually contained a high proportion of organic material. An example is shown in Fig. 3C. Most particles were only partially soluble in water vapour and if floated on water, residues remained. Of the organic vapours, diethylether was the most effective in dissolving the particles and resulted in wide rings denuded of shadow and extensive recrystallisations when the solvent evaporated. Methylbutylketone and cyclohexane vapours affected most particles but not to such a large extent and did not lead to recrystallisation. Decane affected many of the particles but usually to a smaller extent than the other solvents. Fig. 3D shows an example, and the size to which the particle grew is revealed by the surrounding bare patch from which the shadowing material was lifted.

Some free sulfuric acid was present on many of these polluted days, with droplet rings surrounding particles and ammonium sulfate artefacts appearing on the surface after storage. Carbon chains and insoluble electron-opaque materials such as fly ash and clay were present, often embedded in liquid.

The conclusion was that organic liquids had been deposited on whatever particles were present in greater quantities than the sulfuric acid and sulfates commonly seen in aged continental aerosols. Although no nucleation events were observed, it is clear that condensable vapours were present and strongly modified the properties of the aerosol.

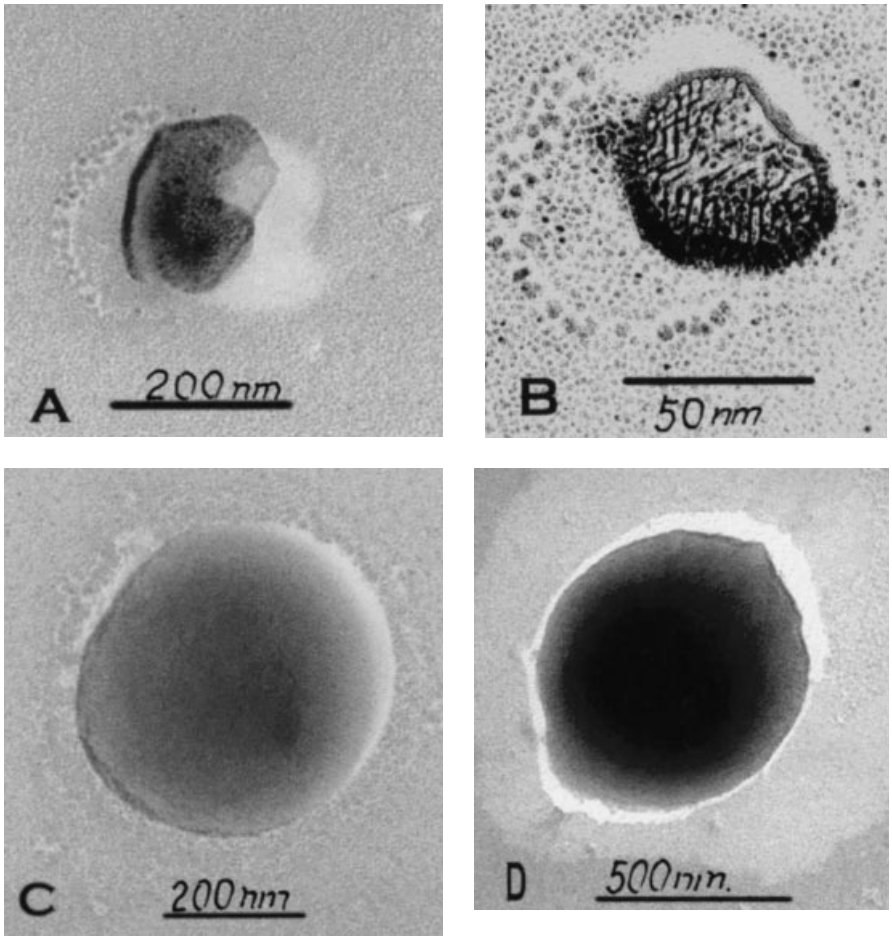

Fig. 3. Particles collected during spring 1998. Scale bar lengths in nm. (A) Solid particle with acid coating. (B) Patterned particle with acid coating. (C) Typical liquid particle that wet the surface. (D) Liquid particle after exposure to decane vapour.

5. Airborne particles in the period 21 March to 16 April 1999

Considerable differences between particle types collected in 1998 and 1999 were found. In the former, particles like those of Figs. 3A, C were numerous in all size ranges. In the 1999 collections these were much less common and no particles resembling Fig. 3B were found although they were specifically sought. Instead some bacteria were present, though they were few. No particles like those of Fig. 2A or crystals like those of Fig. 2B after exposure of particles to decane were found in 1998 but were observed on event days in 1999.

Nucleation events occurred on more than half the days in the 1999 collection period and differences between particle types present on event and non-event days within that period were sought. While it was difficult to get sufficient statistics on each of the many types of particle present, some tentative differences emerged. Those noted only on days with nucleation events were: (1) flat and probably thin crystalline plates (Fig. 4A); (2) particles showing square, leaf-shaped or needle crystals after exposure to decane vapour (Fig. 4D, resembling Fig. 2B); (3) spherical aggregates of small particles like that of Fig. 2A. None of these formed more than a few percent of the total

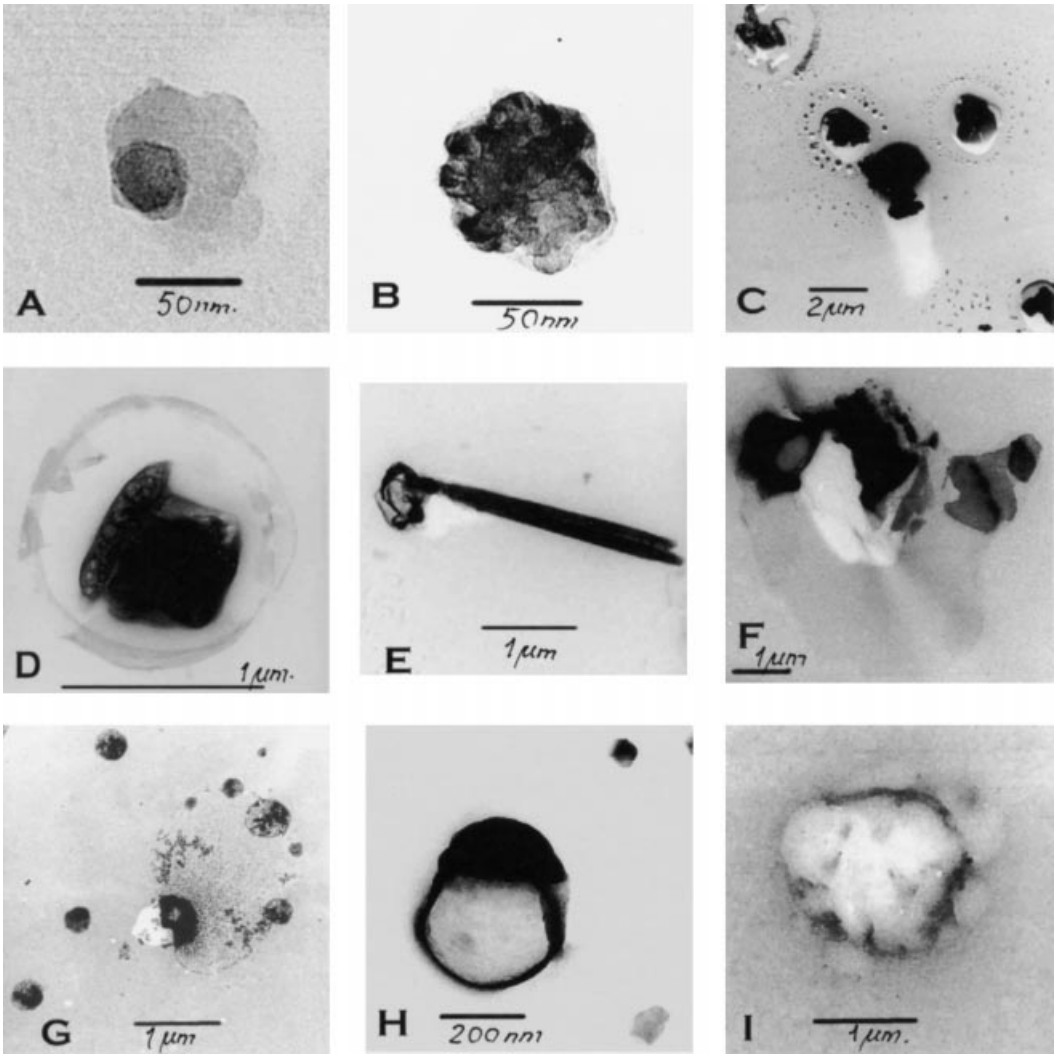

Fig. 4. Particles collected in the free atmosphere, spring 1999. (A) Aggregate of flat crystals, (B) compacted aggregate, (C) particles showing sulfuric acid droplet halos, (D) particle exposed to decane vapour; compare Fig. 2B, (E) crystal formed after exposure to ether vapour, (F) particle floated on flavianic acid revealing amino acid content, (G) particles floated on barium fluoride solution, revealing sulfate content, (H) exposure of a particle to the vapour of osmium tetroxide (the dark areas show osmium deposited by reaction with organic material), (I) particle collected on a wax substrate.

number of particles so that the statistics of a real difference between event and non-event days were poor.

Present on both event and non-event days were more compact aggregates of very small particles like that of Fig. 4A. Some of these were probably carbon chains from combustion sources that had been forced into compact shapes by accretion of liquid material. Particles of >100 nm often showed characteristic droplet rings, or had a sulfate coating (revealed by the barium salt test). Fig. 4C shows a group, at least one of which had a sulfuric acid component judging by the droplet rings. The very electron-opaque particle was either soil dust or (more probably) of industrial effluent origin. Except for a more conspicuous organic

content such particles do not differ greatly from those found in other relatively clean continental areas. As in the case of the 1998 collection, most particles were at least partially soluble in decane, cyclohexane, xylene and ether vapours. A small proportion was completely dissolved in decane (Fig. 4D) whereas in the earlier collections decane-soluble material was only a minor part of the aerosol. Crystallisations after exposure to ether vapour were often spectacular, as in the particle shown in Fig. 4E.

Most of the solid electron-opaque particles >100 nm collected during nucleation events reacted in part with flavianic acid, showing an amino acid content. When floated on water alone most particles were found to have discrete water-insoluble components. The original outline of a particle and its shadow can be seen by the electron-transparent region near the centre in Fig. 4F. The dark stain extending to the lower edge of the photograph represents a widely spread reaction product. Some, or even all, of the dark material could also be reaction product. The more electron-transparent particles had little insoluble material present, did not react with flavianic acid but did leave reaction spots when floated on a solution of a barium salt (Fig. 4G). The relatively uniform residues are consistent with a barium sulfate reaction product and the particles were probably ammonium sulfate, together perhaps with some insoluble components.

Another property of some of the >100 nm particles was to react with osmium tetroxide vapour. The 4% solution in water that was used provided a high humidity so that the hygroscopic portions of a particle were separated from the less soluble components. The latter become extremely electron-opaque by comparison with residues floated on water, showing deposition of osmium by reaction with unsaturated double bonds. Fig. 4H gives an example. It has been printed with such a small exposure that the shadowing material is invisible in order to emphasise the opacity of the osmium reaction.

In 1998 an attempt to use a wax ("Apiezon W-100") having a very low vapour pressure as a shadowing material that caused little heating suggested that particles had volatile components that dissolved the wax. Since the wax is insoluble in water but soluble in hydrocarbons (including aromatics) and in ketones there is the possibility that the particles have volatile components that evaporated before examination. For the 1999 collections, a few grids were prepared that were precoated with the wax. While this produced a relatively poor quality substrate, all particles appeared to have changed the opacity of the wax surrounding them, sometimes out to several diameters of the visible particle. An extreme example is shown in Fig. 3I, collected on an event day. The wax was dissolved out to beyond 1 μm and the solution had evaporated to leave needle shaped crystals. Unfortunately there is no indication of the size of the original particle. These observations lead to the probability that particles in the atmosphere were larger than the sizes indicated by electron microscopy and that either volatile hydrocarbons or ketones were important components.

From these observations it seems that the ambient particles had been less modified by condensed liquids than in the late spring collections of 1998. Some of the distinctive types typical of the soil emission particles (Section 3) were present and these were not seen in the 1998 collections. Volatile components that were lost before examination unless fixed by solution in a non-volatile medium were also present.

6. The soil or leaf litter as a source of nucleating and/or growth material

6.1. The spring maximum of nucleation events

The proposal that penetration of water into the soil causes a release of trapped gases and direct production of particles mainly >100 nm by bubbling appears to be consistent with the observations. If the raw material for nucleation of new particles in the atmosphere was in the released gases or carried on the aerosol, it implies a sharply defined maximum of events when the snow was thawing during the day. Events could occur in summer as a result of precipitation or in winter due to temporary thawing. Kulmala et al. (2001) suggest that the spring maximum is a consequence of an increased incidence at that time of arctic and polar air masses, with which nucleation events were associated. This may well be a contributory factor but it is difficult to believe that their frequency of occurrence should have as sharp a maximum as is observed for the nucleation events.

6.2. *The rôle of dimethylamine (DMA)*

Mäkelä et al (2001) have shown that the DMA ion was present in much larger quantities on event days than on non-event days in particles between 0.1 μm and 1 μm, though in particles <80 nm concentrations were comparable. As DMA has a boiling point of 7°C, the detected ion must have been present in its reaction products. Kulmala et al. (2000) have suggested that initial particle formation is a result of ternary homogeneous nucleation of sulfuric acid, ammonia and water vapour. DMA has similar chemical properties to ammonia but has lower volatility and a larger molecular size. It therefore seems possible that it might have been involved in a similar ternary nucleation scheme in addition to a role of its reaction products in particle growth.

The comparable concentrations of DMA on particles of $<\sim 80$ nm on both event and non-event days is in contrast to its greatly enhanced concentrations on particles of 0.1 μm–1 μm only on event days. In the Arctic and polar air masses associated with event days, the aerosol in that size range was acidic (Section 5) and DMA would have reacted with the acid. In the warm polluted conditions of non-event days in 1998, free sulfuric acid was also present on large particles (Section 4). Here the low concentrations of DMA on those particles could be attributed to low concentrations of DMA and its preferential attachment to more acid small particles. (No evidence is available that they were more acidic.) Since the snow had gone and the soil was becoming dry, a reduced emission is consistent with the water penetration hypothesis of emission from the soil.

6.3. *The hygroscopic growth factor (HGF) diurnal cycle*

Hämeri et al. (2001, this issue) have described the diurnal cycle of hygroscopic growth factors for particles of 10–20 nm diameter during the Biofor campaign. It was similar on event and non-event days. A rise in HGF began soon after sunrise, reaching a flat maximum just after noon, decreased slowly until near sunset and then decreased rapidly. The curves were in fact almost exactly anti-correlated with the diurnal cycle of soil temperature shown in Fig. 1. During nucleation events there was a very large increase in concentrations of 10–20 nm particles that had grown rapidly from the nucleated particles. The unchanged diurnal cycle implies that their HGFs were similar to those of particles of the same size at the same time on non-event days.

The diurnal cycle could be explained by a changing balance in the concentrations of two types of condensing vapours, one that was hygroscopic and one that was not. Soil-emitted compounds that produced hygroscopic condensable vapours would be a maximum during the morning and early afternoon. Janson et al. (2001) have shown that terpene oxidation products should be a maximum at night. If they have low hygroscopicity the proposed changing balance could result.

Kulmala et al. (2001) state that the similarity of the diurnal cycle of hygroscopicity is a clear indication of the separate processes leading to nucleation and condensation. This is not necessarily true. A condensable vapour formed by reaction of a soil-emitted and an ambient gas might always be present in sufficient concentration for significant condensation on existing particles but only present in sufficient concentration for nucleation when the soil-emitted gas concentrations were higher than usual, for example when displaced by water caused by melting snow. However, the nighttime reduction in hygroscopicity was never accompanied by nucleation events and was certainly due to a different condensable vapour.

Examining the ions found by Mäkelä et al. (2001) on the aerosol that were more numerous on event days and that could have been associated with hygroscopic compounds we have: (1) ammonium sulfate, (2) a reaction product of dimethylamine and an acid such as sulfuric, methanesulfonic or volatile organic acids, and (3) the ammonium salts of formic and acetic acids, both of which are deliquescent. (1) can be ruled out because of known slow rates of growth.

6.4. *Compounds carried on aerosols*

While reactive gases are the most probable source of nucleation and growth material produced by decomposition of organic matter in the soil, the possible role of volatile material carried in a slowly evaporating aqueous solution on the aerosol produced at the same time should not be overlooked. Leck and Bigg (1999) showed for example that the amino acid L-methionine when

carried on hygroscopic particles and irradiated with ultraviolet light can lead to particle production. As the tests described in Section 5 showed, amino acids were present on the particles. They did not however, determine which ones. Mopper and Zika (1987) have shown that of the 20 common amino acids only L-methionine is usually found in precipitation in its oxidised form, so that it may be the only one that undergoes chemical transformations in the atmosphere.

7. Conclusions

Observations of the aerosol produced in an enclosure over the snow suggested strongly that displacement by water of gases produced by decomposition of organic matter in the soil had produced them, probably by a bubbling process. The compounds contained in the gases or located in the initially present aqueous phase of the particles are a potential source of nucleating material. If soil and leaf litter are indeed the sources of some of the components of compounds that lead to particle nucleation and growth and water penetration the key to their release, then a very much larger area of the northern hemisphere than this Finnish forest may be involved in modifying the ambient aerosol. It depends on whether the production is peculiar to a Scots pine forest or the understory species of this particular forest, or whether it applies to a much wider variety of vegetation. If the view presented here that breakdown of polymers and proteins provides the ingredients for nucleation, then modification of the aerosol by soil emissions may be almost a worldwide phenomenon. It would however be most noticeable in spring in places where vegetation was covered by snow and thawing allowed daily penetration by water. Elsewhere, liberation would rely on precipitation. Nucleation and growth of the particles would then rely on appropriate timing of the precipitation, sunshine immediately following the precipitation and a following sudden mixing with a cleaner overlying layer of the atmosphere. Achieving all these requirements would probably severely limit the number of occasions on which nucleation events could occur.

8. Acknowledgment

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