PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Ultrafine particles in the atmosphere: introduction

The Royal Society

Phil. Trans. R. Soc. Lond. A 2000 **358**, 2563-2565
doi: 10.1098/rsta.2000.0668

10.1098/rsta.2000.0668

Ultrafine particles in the atmosphere: introduction

City life, mass transport, and mass production enable us to enjoy a civilization both prosperous and offering freedom to travel, but the emission of exhausts into crowded settlements causes urban air to be full of particles which find their way into our lungs and thence into our bodies. Thus, modern governments find it necessary to monitor and try to control the particulate content of the air we breathe.

Over the past decade, overwhelming evidence has accumulated indicating that airborne particles exert a range of adverse effects upon health. These findings came first from epidemiological studies relating population health to airborne particle concentrations. There is a remarkable consistency of effect between different geographic locations, showing a correlation with the incidence of respiratory and cardiovascular diseases. Initially, these findings were received with some scepticism, because there appeared to be no plausible biological mechanism. Toxicological studies then got underway which have revealed a range of mechanisms whereby airborne particles can damage human health. Such studies tend to show that particles become more toxic per unit mass as their size decreases. Thus attention is focused upon surface area or particle number per unit mass, rather than mass fraction, and one is led to consider 'ultrafine particles', those of effective diameter less than one-tenth of a micrometre.

It is only relatively recently that particles in such a size range have received serious attention. The first problem is to characterize them. The first session of the Discussion Meeting tackled this problem. Not only is it necessary to look at overall shapes and sizes, but the chemical composition needs to be known. It seems that quite firm conclusions can be drawn, from studies in quite different locations. Ultrafines account for a very large proportion of the number of particles in the atmosphere, although only a modest proportion of the surface area, and a minute proportion of the mass. Although transport is the main source of them, interesting new results show that even in remote marine atmospheres ultrafine particles are formed, which grow to become nuclei for cloud condensation. In urban environments, the particles are predominantly organic compounds in nature, with further contributions from elemental carbon, trace metals, sulphate, nitrate, and ammonium. It is noteworthy that modern physical techniques are now able to look at particles of nanometre size, and analyse them, and one can expect further technical developments to enhance this capability. It appears that ultrafine particles in engine exhaust comprise two families: the larger ones from the formation of solid carbonaceous particles during the combustion process, and the smaller ones from gas-to-particle conversion processes during dilution of exhaust gases. Control of dilution can influence the relative proportions of the two families of particles.

What are the major sources of ultrafines? The second session explored the answers to this question. Gas-to-particle conversion—that is, nucleation in a supersaturated atmosphere—is one source. The nucleation of sulphuric acid requires a third species such as ammonia to explain the observations. Extraordinarily detailed models can be constructed using the chemistry once it is elucidated, from which it is possible to predict the formation of sulphates from sulphur dioxide oxidation as well as of secondary organic particles produced by the oxidation of both natural and anthropogenic organic compounds. When combined with predictions of long-range transport of air masses, such models display an impressive capability to predict local sulphate concentrations deriving from distant sources in the UK and in continental Europe. On the other hand, emission from internal combustion engines caused by exhaust dilution processes can be explained in detail by nucleation processes involving sulphuric acid and subsequent condensation of organic matter largely coming from lubricating oils. By control of the sulphur content it appears possible to suppress the formation of such particles and to manipulate particle size distributions through vehicle design and fuel composition. However, from open flames fed by hydrocarbon combustion one sees solid carbonaceous particles which ultimately produce ultrafines of up to 5 nm diameter, composed of elemental carbon. These coagulate and support the condensation of further primary particles, growing ultimately into diffusion-limited aggregates of clusters. Do these processes occur in the workplace, and if so, how can they be controlled? How might it be possible to set out an ultrafine particle convention for use alongside other particle size conventions to use in regulating exposure within the workplace? The answer to this question depends upon the potential health risks associated with the various types of ultrafines, and leads therefore to the question of particle toxicology and its mechanisms, the subject of the third session.

Re-examination of the patterns of deposition of very small particles in the respiratory system has led to an appreciation that, while ultrafine particles deposit well in the distal parts of the lung, even smaller particles, less than 10 nm in diameter, do not: most deposit in the upper airways. The interaction between such particles and the surface-active material that lines the respiratory tract has been studied, and one can see that the low surface tension produced by a surfactant film aids particle transfer through the liquid lining layer. Perhaps most remarkably, ultrafine particles have been shown to have unusual toxicological potency. Particles of titanium dioxide, aluminium oxide and carbon black of less than 50 nm in diameter have all been shown to be much more toxic per unit mass than similar particles ten times larger. The reasons for this property are being explored. The smallest of such particles may display extraordinary surface chemistry which arises from geometrical constraints on the packing of ions in what amounts more to a 'particulate molecule' than a section of bulk material. Thus there is not only high specific surface area, but surfaces of special composition which may be rich in metallic species and play an important part in free radical generation: an effect displayed by oil flyash, but not in that produced by small particles of carbon black or latex, which are metal-free.

When it comes to studying the effects of ambient aerosol upon the health of populations, one can show that variations in daily counts of events such as deaths and hospital admissions are related to day-to-day changes in the mass concentration of particles. The fourth and final session concerned itself with detailed epidemiological studies which produce robust confirmation of these effects. The view that there is a causal association between mass concentration of particles and ill-health is now generally accepted. Recent studies have revealed differences in the magnitude of the effects between cities, for a given mass concentration. Why does one find this variability? In some studies, number concentration of particles is found to be more strongly related to ill-health than mass concentration. Other studies confirm this by showing that mass concentrations of smaller particles may be better correlated to health effects than those of larger particles. A limited number of cohort studies suggest that long-term exposure to even low concentrations of fine particles ($PM_{2.5}$ or sulphate) may be associated with reduced life expectancy.

Thus, although ultrafine particles contribute very little to the mass concentration of the ambient aerosol, they may contribute disproportionately to its toxicity. The 'ultrafine hypothesis' seeks to explain at least some of the reported associations between mass concentration and indices of ill-health by suggesting that mass concentration is a surrogate for the number of ultrafine particles. If true, this view will have far-reaching implications: control of mass concentration without control of the ultrafine component will have little effect in reducing damage to health. The study of ultrafine particles in the atmosphere, and their pathways into the human body, is a new and vital multi-disciplinary subject which will attract intense study over the next few years.

L. M. Brown
N. Collings
R. M. Harrison
A. D. Maynard
R. L. Maynard

MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES
PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A