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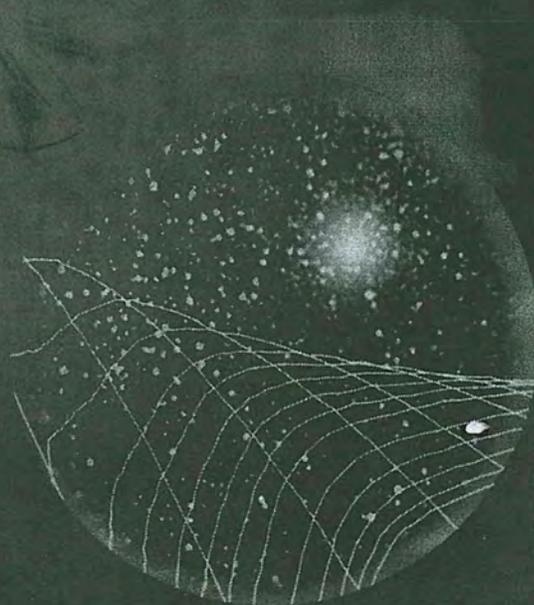
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Ultrafine Particles in the Atmosphere

Imperial College Press

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ULTRAFINE PARTICLES IN THE ATMOSPHERE

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PREFACE

The past decade has seen mounting evidence that atmospheric particles are more damaging to health than previously thought. Epidemiological studies relating population health to airborne particle concentrations provided some of the first indications of a hitherto unsuspected toxicity. 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. However toxicological studies have since indicated a range of mechanisms that underpin the epidemiology, whereby airborne particles may damage human health. Many studies have now shown that some particles become more toxic per unit mass as their size decreases. Thus attention is focused upon particulate surface area or 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 micrometer.

In March 2000 The Royal Society (London) hosted a multi-disciplinary discussion meeting to address issues surrounding ultrafine particles in the atmosphere. Eminent researchers from a wide range of disciplines met together over two days to consider the current state of our knowledge and understanding of ultrafine aerosol generation, characterization, transportation, exposure and toxicity. The result was a comprehensive overview of what we know, and what information is yet needed, about ultrafine particles and how they potentially impact our health. This collection of papers is based on the lectures given at the meeting, and likewise comprehensively documents the current state of affairs regarding ultrafine particles in the atmosphere. Chapters 1 to 3 consider the characterization of ultrafine particles. Chapters 4 to 8 follow on by considering the sources of ultrafine aerosols. The remaining chapters deal with the health effects associated with ultrafine particulate exposure: chapters 9 to 13 focus on the toxicology of ultrafines, while chapters 14 to 16 conclude by considering the epidemiology of ultrafine aerosol exposure. Sadly, Professor Glen Cass, author of chapter 2 on the chemical composition of atmospheric ultrafine particles, passed away prematurely in July 2001.

It is only relatively recently that particles in the ultrafine size range have received serious attention. The first problem is to characterize them. Chapters 1 to 3 address this issue. Not only is it necessary to look at overall particle shapes and sizes, but the chemical composition also needs to be determined. It seems that quite firm conclusions can be drawn, from studies in a number of 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 motor transport vehicles represent the main source of them in urban areas, 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 appear to be predominantly organic compounds in nature, with further contributions from elemental carbon, transition metals, sulphate, nitrate, and ammonium. It is noteworthy that modern physical techniques are now able to look at particles of nanometre size, to analyze them, and one can expect further technical developments to increase this capability. It appears that ultrafine particles in engine exhaust can be divided into 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. Confounding factors such as dilution can influence the relative proportions of the two families of particles.

What are the major sources of ultrafines? Chapters 4 to 8 explore 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 observed nucleation. Detailed models can be constructed using the chemistry of sulphuric acid, which is elucidated, from which it is possible to predict the formation of particles from sulphur dioxide oxidation as well as of secondary organic aerosols, produced by the oxidation of both natural and anthropogenic hydrocarbon compounds. When combined with predictions of long-range transport of air masses, such models display an impressive capability to predict sulphate concentrations deriving from distant sources in the UK and continental Europe. On the other hand, emissions from internal combustion engines caused by exhaust dilution processes can be explained in detail. 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 consumption. However, from open flames fed by hydrocarbon combustion one sees solid carbonaceous particles a few nanometres in diameter, comprised of elemental carbon. These coagulate, growing ultimately into diffusion-limited aggregates of smaller 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 chapters 9 to 13.

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 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 to a 'particulate molecule' rather than a section of bulk material. Thus there is not only high specific 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 fly-ash, 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. Chapters 14 to 16 are concerned with detailed epidemiological studies which produce robust confirmation of these effects. The view that there is a causal association between mass concentra-

of particles and ill-health is now generally accepted. However there is evidence suggesting that the association is stronger with smaller-diameter particles. 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 are 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 or surface area 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. With increased awareness of ultrafine aerosol exposure in the environment, workplace and in the home, and in particular with the emergence of aerosol-based nanotechnology, this is an area of research which will no doubt attract intense study in the next few years.

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