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Particles from internal combustion engines—what we need to know

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Internal combustion (IC) engines are a major contributor to the total particulate emissions inventory, especially in urban areas. Recent epidemiological studies suggesting links between fine particles and negative health effects have sparked an increased interest in this subject. While particulate emissions from IC engines have been the focus of research for many years, a great deal of information crucial to our understanding of this subject still remains unknown. In this paper the authors address some of these unknowns, focusing primarily on the process and consequences of aerosol dilution strategy. The thermodynamics of dilution are considered, and the inadequacy of conventional constant-volume sampling dilution tunnels for ultrafine particle characterization are demonstrated using experimental data. Finally, time-resolved data demonstrating the variation in concentration of pollutants in a vehicle moving in traffic are used as an example of the difficulties in setting legislation aimed at controlling exposure to ultrafine particles.

Keywords: nanoparticle; aerosol; dilution; thermodynamics; nucleation; condensation

1. Introduction

Without doubt the most important fact to establish with regard to particulate emissions from internal combustion (IC) engines is the exact relationship between emission, exposure and subsequent health effects. This relationship is not very well understood currently, and it seems unlikely to be resolved in the near future, especially with regard to the long-term health effects of exposure to ultrafine particulate matter. In the case of IC engine emissions, debate continues with regard to what the important parameters are which should be examined (e.g. particle size, number, surface area, mass, composition, etc.) in terms of measurement, control and legislation. No general agreement yet exists as to what the most appropriate techniques and equipment (if they even exist) for the dilution and subsequent measurement of IC engine exhaust particulate matter might be. It is unclear whether much of the data collected to this point are representative or even applicable for the characterization of particulate exposure with respect to health effects. Consequently, there is a low level of confidence concerning our ability to determine appropriate limits for the legislative control of vehicle particulate emissions.

What do we know at present?

(a) There is no doubt that IC engines are responsible for a significant fraction of total particulate matter present in the atmosphere, especially in urban areas

(UK QUARG 1996). The fraction attributable to mobile sources depends on how the particles are counted, a recurring dilemma.

(b) It is now accepted that both the manner in which a vehicle's exhaust is diluted (if at all) and the technique and instrumentation used for subsequent measurement of the exhaust aerosol can (and usually do) have profound effects on the measured character (e.g. size, number, composition) of the aerosol.

(c) It can be exceedingly difficult to establish adequate repeatability between repeat tests, let alone different laboratories, particle levels sometimes exhibiting a large, seemingly random, element.

(d) The widespread use of particle traps will reduce diesel vehicle particulate emissions very significantly.

(e) Low-sulphur fuel will reduce particle emissions.

At present, vehicle particle emissions legislation is based solely on the mass emission (i.e. PM_{10} and $PM_{2.5}$) of particles collected on a filter directly from a standard constant-volume dilution tunnel. This is a standard of measure which, in effect, exempts ultrafine particles from legislated control. This 'exemption' of ultrafines is due to the negligible contribution of ultrafines to total particle mass, and is compounded by the poor representation of atmospheric dilution obtained with conventional constant-volume dilution systems used in making such measurements. Ultrafine particles in the atmosphere that result from vehicle emissions can form both on short time-scales (e.g. through condensation and nucleation as exhaust gas exits the vehicle tailpipe and mixes with the atmosphere) and on much longer time-scales, e.g. due to photochemical processes.

In this context it is tempting to simply require emission levels to be as low as technically feasible, on the basis that there is no threshold level at which harm is zero; and this, in essence, is the route being followed as far as gaseous vehicle emissions. There are significant and fundamental reasons for not following this route with respect to particle emissions. Perhaps the most compelling as far as IC engines are concerned is the persistent difficulty associated with the definition of appropriate test procedures for dilution and sampling.

In the case of gaseous emissions, the composition of legislated species (e.g. HC, CO, NO_x) remains virtually unchanged during mixing and dilution in the atmosphere, while secondary processes (e.g. formation of photochemical smog) occur on relatively long time-scales. On the other hand, it is well known that upon leaving the tailpipe, the particle size spectrum and composition changes dramatically on time-scales ranging from milliseconds to days, depending on a number of factors including rate of dilution, final dilution ratio, atmospheric conditions (temperature, humidity, background particle levels, etc.; see Abdul-Khalek *et al.* (1999, 2000) and Graskow *et al.* (2000)). In the case of exposure to nanoparticles ($d_p < 50$ nm), the dose rate that the individual is subject to decreases strongly as the separation (both in terms of distance and time) between the individual and the emission source is increased (due to agglomeration and convective and diffusive dispersion and dilution). Consequently, exposure to vehicle-borne nanoparticles may vary wildly from person to person, depending on an individual's 'lifestyle'.

Progress in assessing the importance that should be attached to such considerations can only be made if the relative health effects are better understood. Recent studies (Donaldson *et al*. 1996, 1998; Ferin *et al*. 1992) have highlighted the possibility that current legislation may actually increase health risks if it was found that nanoparticles were significantly more harmful than large particles, since it is essentially only the latter that are controlled, and minimizing their mass may result in an increase in total number due to the reduction in surface area of carbon adsorbate. Leaving the important questions of whether we are monitoring the appropriate parameters in the environment and how legislation should be progressed, let us focus our attention on the issue of dilution and standard test procedures.

2. Current test procedures

The current standard test procedures (i.e. those required by law to be used in assessment of particulate emissions) are designed specifically for the measurement of particle mass emissions. In the current standard method, the entire engine exhaust flow is directed into a constant-volume dilution tunnel, where the exhaust is mixed with particle-free dilution air. In such systems, the total flow of the engine exhaust and dilution air is held constant. Since the amount of engine exhaust flow changes according to different engine operating conditions (exhaust flow increases roughly in proportion to engine speed for diesel engines, and in proportion to power in gasoline engines), the dilution ratio also changes; typical dilution ratios for constant-volume dilution systems range from 3 to 15, depending on the engine and operating condition. A sample of this diluted aerosol is then collected on a filter, which can subsequently be analysed to determine the mass and soluble organic fraction of the emitted particles. If particle losses in the dilution and sampling systems are ignored, then the mass collected is largely independent of the details of the dilution process. This is because the total mass of particles collected in such a way is overwhelmingly dominated by relatively large ($d_p > 100$ nm) carbonaceous particles that are formed within the combustion chamber, and which therefore remain virtually unchanged by the dilution process. Consequently, the current methods are adequate for determining compliance with the current mass-based legislation (so long as sufficient care is taken with regard to particle losses and gains during the measurement).

However, if it proves to be correct that much of the negative health impact from particles is due to ultrafines (Donaldson *et al*. 1996, 1998; Ferin *et al*. 1992), it seems that a change in legislative emphasis away from mass and toward number or surface-area weighting is likely. The current method for measuring mass-based particle emissions is totally inappropriate for assessing emission of ultrafine particles, since these particles contribute negligible mass, even if present in extremely high concentrations. If such a change in standards were to occur, then it is difficult to overemphasize the difficulties in defining consistent, representative test procedures. The lack of reproducibility in measurements pertaining to the smallest particle size ranges between laboratories is legion.

The reason for this variability in results is not difficult to explain. Nanoparticles are largely generated during the dilution process as the hot exhaust gas mixes with cool ambient air. The primary mechanism for nanoparticle formation during dilution is homogeneous nucleation of sulphuric acid, onto which either volatile organic compounds or their oxidation products condense. All of these components normally

remain in the gas phase at exhaust gas temperatures. Nucleation is, of course, a notoriously nonlinear process, which can be exquisitely sensitive to a number of variables in the dilution process. A number of these variables have been shown to have a significant effect on nanoparticle production, including overall dilution ratio, rate of dilution, turbulence intensity, mixing length-scales, dilution air temperature, humidity, and background particle concentration (Abdul-Khalek *et al*. 1999, 2000). In addition to the variability introduced by dilution, particle formation is also significantly affected by the exact nature of the exhaust gas (temperature, amount and composition of particles and gas-phase particle precursors), which itself is strongly dependent on the fuel and lubricating oil used, as well as the engine operating conditions, mechanical condition of engine components, etc.

Given this, and the practical difficulties of producing an appropriate test procedure that determines the representative nanoparticle production of a given engine/vehicle combination, it may be worthwhile to examine the possibility of developing a standard predictive model, the input for which is the undiluted exhaust gas composition itself. If the exhaust gas composition relevant to its particle-forming potential can be measured, then one might use those data to apply predictive models based on a wide range of ambient and dilution conditions (assuming that these can be modelled effectively). This would yield emissions information for a much wider range of conditions than is practical to test experimentally, either in the laboratory or on the road.

In light of the extreme dependence of particle formation on the dilution process, one must take great care in creating a dilution system which provides dilution conditions that are representative of those which occur in the real world. While the standard constant-volume dilution method described above is adequate for making mass-based particle measurements (due to the insensitivity of large particles to dilution conditions), such a system is completely inappropriate for use with number-based (e.g. scanning mobility particle sizer (SMPS) and condensation particle counter (CPC)) measurements. As stated earlier, typical dilution ratios for constant-volume dilution systems range from 3 to 15. Under such circumstances the dilution ratio never reaches a point where the processes of nucleation, condensation or agglomeration are effectively arrested, as they are in the atmosphere. In fact, whereas the nuclei mode is normally prominent in measurements of emissions from modern diesel engines measured both on the road and using non-constant-volume sampling (non-CVS) dilution systems, the nuclei mode is often conspicuously absent in measurements made using the CVS dilution system (see experimental section below). This is because under many conditions, the dilution process in CVS tunnels is insufficient to trigger nucleation, which would normally occur during the process of dilution in the atmosphere. While this makes little difference in terms of measured particle mass emissions, it can have an overwhelming influence on particle number, potentially resulting in several orders of magnitude error in the estimated particle number emissions.

In addition to the low dilution ratios, it seems unlikely that the dilution process in the current standard dilution tunnels are comparable with those encountered in atmospheric dilution; the resulting change in the mixing process may have profound implications for the thermodynamics of particle formation (see discussion below). Finally, since the dilution ratio changes between different operating conditions, the resulting particle size distribution may change from condition to condition, even if

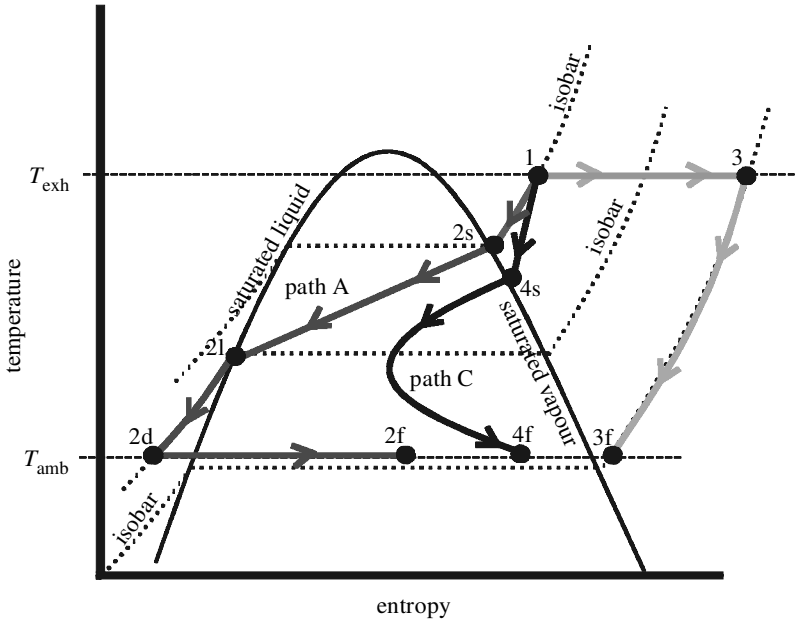

Figure 1. Temperature–entropy diagram showing different paths of dilution.

exhaust-gas composition remains identical. Consequently, such a system is unsatisfactory for number-based measurement of ultrafine particles.

Abdul-Khalek *et al*. (1999, 2000) highlighted these issues by the design of a two-stage dilution system, in which the effect of dilution ratio, temperature, relative humidity and residence time between dilution stages can be studied. The results showed that total measured particle number emissions from a diesel engine at a set operating condition could be changed by two orders of magnitude as a result of modest changes in dilution conditions.

In summary, it is argued that the production of nanoparticles is primarily driven by nucleation of one or more precursor species (of which, sulphate is believed to be most important) that exist in the gas phase in hot engine exhaust. Particles are formed as these species are forced into a state of supersaturation during dilution as exhaust is cooled and mixes with ambient air. After the dilution ratio has exceeded some critical value, dynamic particle formation and growth processes (nucleation, condensation, agglomeration) effectively cease to operate due to a lack of driving potential at high dilution ratios. The total number of particles produced during dilution is extremely nonlinear and is highly sensitive to detailed conditions of the dilution process itself. Based on a simple examination of particle formation and the dilution process, it can be clearly seen that standard constant-volume dilution systems are unsuitable for measurement of ultrafine particulate matter. Such systems may drastically underrepresent the total number of ultrafine particles that is likely to be emitted from IC engines under real-world dilution conditions.

3. Thermodynamic paths of dilution

Thermodynamically speaking, there are a number of paths that the exhaust can take during dilution, depending on the details of the dilution mixing process. The

details of the thermodynamic path taken can have profound consequences in terms of particle formation in the diluting exhaust. Figure 1 is a temperature–entropy (T–s) diagram which considers the thermodynamic state of a particle precursor species (e.g. sulphate) during dilution. State 1 on this diagram represents the species at its starting point, as a superheated gas in the exhaust exiting the tailpipe. We will begin by examining the fate of this species under two limiting cases of dilution based on different mixing strategies.

In the first case (path A), convective mixing is poor, and consequently the aerosol is cooled but not diluted by the ambient air. This is the case when the Lewis number (Le, defined as the ratio of thermal diffusivity to mass diffusivity) is much greater than unity ($Le \gg 1$). This situation may be approximated, for example, when turbulence and mixing is very low, e.g. in a vehicle that is moving slowly or stopped at idle. Since no mass transfer occurs in this situation, the vapour will cool at constant pressure until it becomes saturated at state 2s. As the species is cooled further, the vapour pressure will drop as the species first condenses on existing nuclei, then nucleates to form new particles. Eventually, a significant fraction of the vapour will condense or nucleate (state 2l), and the species enters the sub-cooled liquid region. The remainder of the vapour follows the saturated vapour line (not shown). At point 2d, we allow the aerosol to be diluted until it reaches the final state 2f, where it is at thermal equilibrium with the environment (the exact location of state 2f being dependent on what final overall dilution ratio is assumed).

The next limiting case to consider is one where dilution occurs isothermally (requiring a heat input), moving the superheated vapour from state 1 to state 3 (path B). Following dilution, the species is allowed to cool at constant pressure to the final state 3f, where it is at thermal equilibrium with the environment. In this case, the species remains in a superheated vapour state at all times, thus eliminating the possibility of particle growth or formation due to condensation or nucleation of this species.

Under real atmospheric dilution conditions, dilution and cooling occur simultaneously ($Le \sim 1$; path C), taking the species from superheated vapour at state 1 to saturated vapour at state 4s. Cooling and dilution then continue, bringing the species to its final state 4f. The exact thermodynamic trajectory which the species follows between states 4s and 4f will be determined by the intensity and scales of mixing during dilution; as mixing intensity increases, the trajectory will shift to the right, resulting in lower peak saturation ratios. This reflects the reduction in diffusive heat loss between pockets of diluting exhaust precursors and the cooler dilution air (Davenne *et al.* 2000). Under conditions of intense mixing, dilution may become adiabatic, possibly avoiding a saturated vapour state altogether.

Although the illustration of the three dilution scenarios described above is highly qualitative, it does serve to demonstrate how the thermodynamic state of a particle precursor species may be affected by the dilution process. Obviously, if one could dilute in such a way as to avoid reaching the saturated vapour stage (e.g. with isothermal dilution or very intense mixing), then nucleation could be prevented altogether, resulting in a dramatic reduction in nanoparticle emissions. Even if it is impossible to completely avoid a saturated vapour state, one may still manipulate the mixing process in such a way as to minimize saturation ratio and, thus, particle formation. One important point to note regarding figure 1 is that between the initial and final states (i.e. state 1 to 2f/3f/4f) the species is not likely to be in a state of

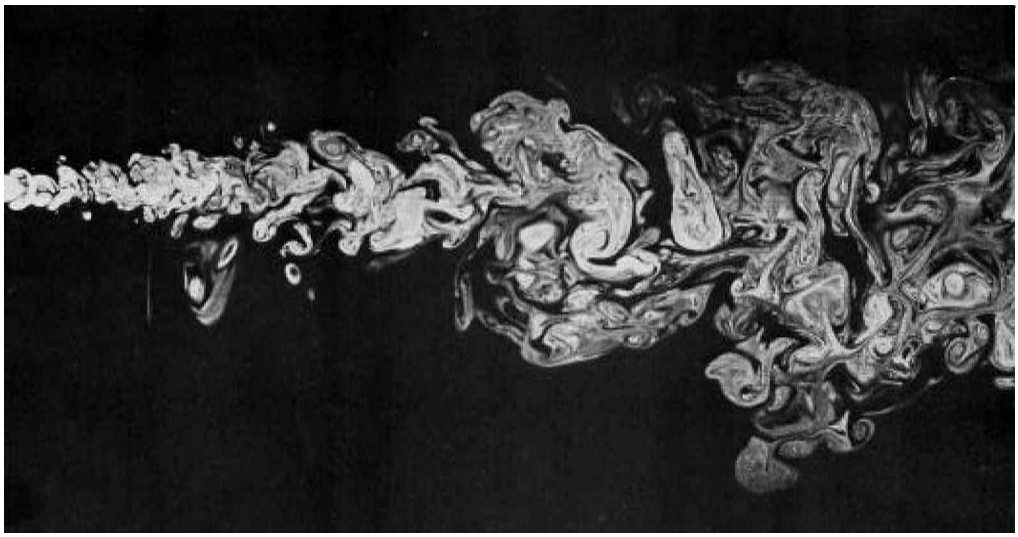

Figure 2. Mixing plume of a turbulent jet (Van Dyke 1982).

thermodynamic equilibrium. Consequently, condensation and nucleation processes may become time-limited. If mixing intensity is high, then the amount of time which a species spends at high saturation ratios may be short enough to avoid nucleation (or condensation) completely.

Curiously enough, entropy maximization is key here: the number of particles formed during dilution is inversely proportional to the final entropy of the diluted aerosol. Because the species has a lower state of entropy in particle (liquid) form than it does in gas form (from figure 1, we see that saturation ratios increase in the vapour dome as entropy decreases), nucleation of particles will result in a net decrease in entropy. Consequently, if we assume that the final dilution ratio is identical for all dilution scenarios, then the dilution path with the highest final entropy should produce the fewest particles. The price which is paid for higher entropy is the energy required to supply heat (isothermal dilution, path B) or to produce rapid turbulent mixing (path C).

The actual mixing process is always, in practice, turbulent (in experimental as well as real-world dilution), and inhomogeneous on a micro scale (Davenne *et al.* 2000). A picture of a turbulent plume (figure 2) illustrates this point; some of the vapour at the extremities of an eddy is micro mixing with short time-scales, while other vapour at the centre of an eddy is cooling before mixing. This is an essential difficulty, and experiments that attempt to mimic real-world dilution processes have to address the issue of mixing scaling. In addition, the question of exactly what level of mixing is representative of atmospheric mixing arises; given that vehicles operate under a wide range of speeds and under widely varying atmospheric conditions (temperature, humidity, wind, background particle concentration, etc.), this is likely to be a question for which there is no simple answer.

It might be argued that as current significant particle emitters (diesel engines, perhaps some types of gasoline engines, maybe other engine types depending on how the standards progress) will in the future operate with low sulphur fuel and be fitted with particle traps, IC engines will cease to be a significant contributor to the particle

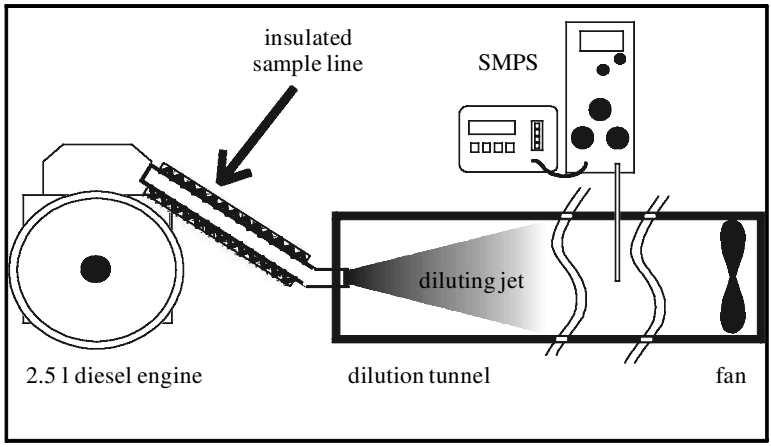

Figure 3. Dilution tunnel experiment schematic.

emissions inventory. There is no doubt that particle mass will be very significantly reduced by these and other means (higher injection pressures in the case of diesel engines for example), though the effect of these measures on number emissions may not be so dramatic. Indeed, nanoparticle formation is itself very significantly reduced by any reduction in fuel sulphur, though where a finite level of engine oil consumption occurs (as in the diesel engine), sulphur-related fine particle generation is likely to remain significant. Such considerations focus attention back onto identifying test procedures that will appropriately assess the fine particle problem.

4. Experimental

We present here some results obtained during an investigation to examine real-world dilution processes. Particle size distributions emitted from a diesel engine have been measured using a dilution system which has a dilution ratio sufficient to approach atmospheric dilution conditions. Figure 3 shows the apparatus used for this. The engine used was a 2.5 l displacement direct injection four-cylinder diesel, using standard 300 ppm sulphur diesel fuel; engine loading was accomplished through the use of a water brake dynamometer. The exhaust from one of the cylinders was taken to the dilution tunnel via a short (1 m) heated sample line, which was maintained at 200 °C. The exhaust from a single cylinder was used, as this ensured a minimum overall final dilution ratio of approximately 100:1 in the tunnel that was used. When mixing is complete at this dilution ratio, particle evolution (nucleation, condensation, agglomeration) can be assumed to effectively be halted. The dilution tunnel itself had a square cross-section, of side 0.4 m, with a dilution air flow rate of 0.3 $m^3\ s^{-1}$ (unfiltered ambient air was used), resulting in a tunnel Reynolds number of 10^5. The diluted sample was extracted at a location 4.0 m downstream from the tunnel entrance, allowing the aerosol to become fully mixed with the dilution air.

The objective of this exercise was to measure the resultant particle size distributions under dilution conditions that mimicked those occurring in the environment. Typical results are consistent with those which might be expected on the basis of Abdul-Khalek *et al.*'s experiments (1999, 2000): a significant nuclei mode, not typically observed in a conventional CVS dilution tunnel for such an engine (Rickeard

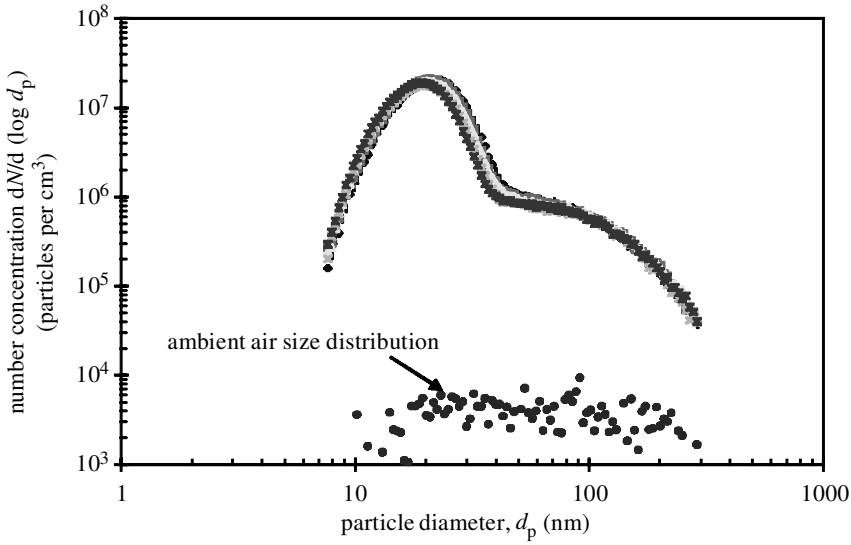

Figure 4. Tunnel-diluted diesel exhaust particle size distribution.

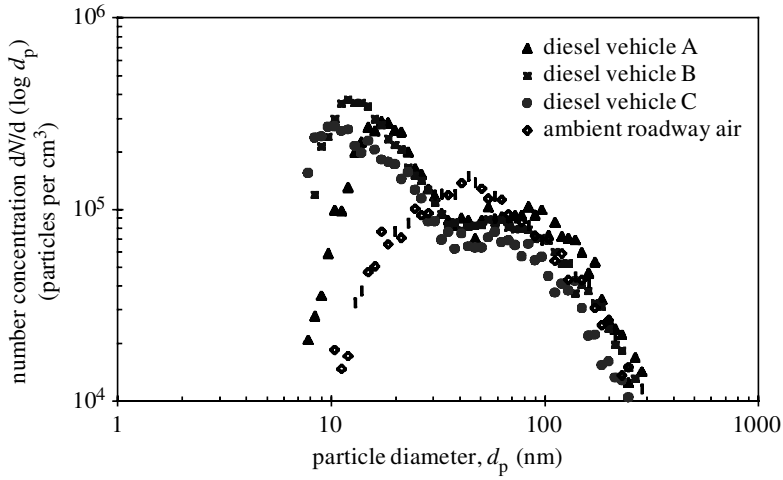

Figure 5. Motorway measurement of diesel vehicle aerosol size distributions (100 km h^{-1}).

et al. 1996; Greenwood *et al*. 1996; McAughey 1997). Figure 4 shows several repeat number-weighted size distributions (measured using an SMPS) measured at a typical engine operating condition (1500 rpm, 7.5 kW). This nuclei mode was consistently displayed over a wide range of operating conditions.

Although this type of experiment is reasonably well controlled, the 'dilution tunnel' was quite massive, even though only 25% of the gas from this (smallish) engine was used. If similar dilution methods were to be used in some sort of standard test method, it seems practical that only a partial sample of the total exhaust flow can be used, and then, as mentioned in the previous section, the question of experiment scaling arises.

In a companion study, an SMPS was mounted in a chase vehicle, and a series of

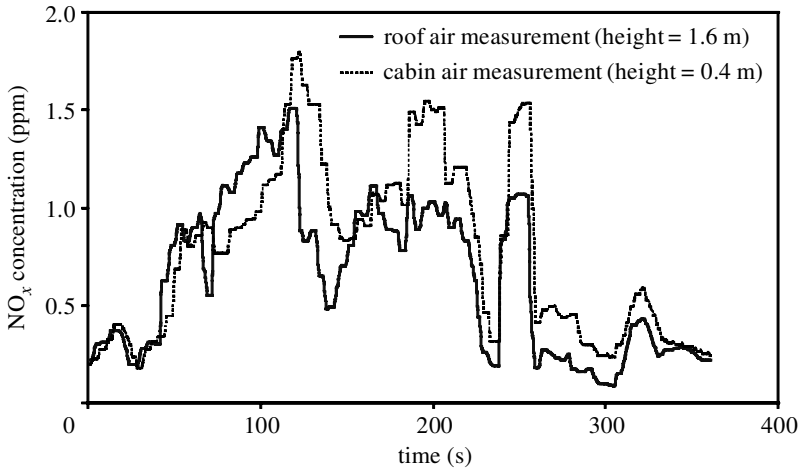

Figure 6. Variation in NO_x concentration above the roadway surface in traffic.

vehicles were followed on a motorway (*ca.* 100 km h^{-1}) at an approximate distance of 100 m. The aerosol was measured at the exit of the chase vehicle's cabin ventilation system, thus the aerosol measured is the same aerosol to which vehicle occupants would be exposed. Of course, such experiments must necessarily sacrifice controlled, experimentally reproducible conditions for real-world data, but the results are revealing (see figure 5). The size distributions measured behind diesel-powered vehicles are similar to those measured in the laboratory using the dilution tunnel (figure 4); as the data in figures 4 and 5 are not corrected for dilution ratio, no inferences should be made on the basis of differences in the absolute value of measured number concentration. Significantly, aerosol emitted from the diesel vehicles contains a prominent nuclei mode; again, not what would typically be measured if the vehicle was tested using a conventional CVS dilution system. Size distributions measured for gasoline-powered vehicles were not discernibly different from the ambient size distribution.

Though not directly concerned with particle measurements, a similar study looking at on-road NO_x emissions showed that there is a significant variation of this pollutant with height above the road surface. In this study, two chemiluminescent NO_x detectors were fitted to the chase vehicle; one detector was used to measure the NO_x concentrations in the air entering the cabin compartment, and the other sampled from a point at the side, and top, of the vehicle. The cabin air was taken from a grill between the bonnet and the front windscreen, and reference to air flow studies over similar vehicles suggests that this air comes from a height of *ca.* 0.4 m above ground level. The high sample point was at a height of 1.6 m above ground level, and to the side of the vehicle, sampling air originating from about this level. All of the data were taken when in traffic—both motorway and town—which consisted of a combination of both diesel and petrol vehicles.

A typical set of results for these experiments is given in figure 6. As this figure shows, while there is a good degree of correlation between the trends in NO_x, the absolute concentration levels exhibit significant variation. Quite significant is the fact that the concentration of NO_x was generally much higher in the cabin ventilation air than it was at a point at the top of the chase vehicle, reflecting the increase in dilution ratio as height above the roadway surface increases. Presumably, similar

variations would be observed in terms of particle concentration at different heights above the roadway. Clearly, this type of anecdotal data begs many questions, but it would seem to have ramifications for vehicle occupants in traffic.

Given that significant fluctuations in exhaust gas composition are observed on very short time-scales both on the road and in the laboratory (Peckham *et al*. 1998; Sutela *et al*. 1999), the question of measurement time response arises. In addition, there is a good deal of evidence suggesting that particle emissions from engines may also exhibit significant fluctuations under steady-state operating conditions (Graskow *et al*. 1998). The problem in measuring short time-scale variations in engine-out emissions is exacerbated by the short time-scales on which particles form and evolve. Particle sizing instruments currently available have time responses which vary from a few seconds upwards (usually much longer); typical aerosol sampling and dilution systems significantly degrade time response even further. If we are to examine particle emission, formation and evolution properly both for steady-state and transient engine operating conditions (e.g. for currently legislated standard drive cycles), we will require instruments capable of measuring particle size on very fast (sub-second) time-scales; such instruments are currently under development.

5. Conclusions

Again, the single most important piece of information that we need to understand is how exposure to particles affects the health of individuals, and the public-at-large in general. This needs to be determined for both acute (short-term) and chronic (long-term) exposures, with the effects of particle size, morphology (surface area) and composition considered. Related to this is the need to understand typical exposure conditions with regard to particle size, number, composition, etc. Exposure will further need to be assessed subject to the dramatic variations that different individuals may be exposed to based on their lifestyle and activities.

In terms of measurement and control of particulate emissions, we need to better understand the process of dilution and how it can affect particle formation. One of the first steps toward understanding this is the study of real atmospheric dilution, outside of the laboratory. Given the wide variety of vehicle designs, vehicle operating conditions, and atmospheric conditions, it will be important to establish the variability in dilution which will need to be simulated in the laboratory. Of course, closely controlled experimental laboratory studies are also needed in order to establish methods whereby these representative conditions of true atmospheric dilution can be simulated practically.

An intimate knowledge of the relationship between dilution and particle formation may also yield insight that will allow particle formation and emissions to be reduced by active on-vehicle manipulation of the atmospheric dilution process itself. Development of instrumentation for the fast measurement of particles will be very important for the study of such formation and dilution phenomena.

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Discussion

M. S. Bingley (*Cobham, Surrey, UK*). Driving in an open-topped sports car demonstrated that exhaust gas went forward over the car. This demonstrated that it was very difficult to determine the manner of exhaust gas dilution in a car. Nevertheless, were you going to conduct experiments, sampling exhaust gas, on a car, on the road?

N. Collings. The car involved in the tests was not open top. The measurements of NO_x concentrations were those that occupants would be exposed to.

C. F. Clement (*Oxon, UK*). The time-scale and sequence of the physical processes of cooling and dilution will control the nature of the aerosol emerging from internal combustion engines. If the cooling occurs before the expansion, vapour will condense on pipe walls and aerosol formed may have time to coagulate out of the ultrafine

size range. With the process of coagulation, it is the condensed mass concentration and, therefore, the amount and rate of dilution which determines the aerosol size. The faster the dilution rate, the more likely the aerosol is to be 'frozen' into ultrafine sizes.

N. Collings. I agree with this comment, and it is an important aspect of the sensitivity of the final spectrum to the dilution trajectory. However, very fast dilution might lead to a smaller ultrafine component if the time for nucleation was short enough. Whether in actual exhausts such very fast dilution is practical is an open issue; a very large quantity of gas (air) would be required to get very fast 100:1 dilution, the order of magnitude required to freeze the processes. As the comment suggests, cooling before dilution might be a better route to ultrafine particle suppression, though the rate of condensation on walls might be less important than coagulation/agglommeration processes.

M. Williams (*DETR, London, UK*). If ultrafine particles are found to be important for regulation, given the sensitivities of their production in exhaust emissions, do you feel that rather than regulating number concentration in emissions, it may be more profitable to regulate their precursors?

N. Collings. I agree with the suggestion that measurement of the ultrafines will be very problematic in practice, and that regulation of the precursors may be the only viable option. A concept of 'ultrafine-particle-forming potential' would seem to be appropriate, much as ozone-forming potential is presently used, where measurements of the exhaust gas composition, especially the different hydrocarbon species, leads, via a model, to the ground-level ozone-forming potential.

L. M. Brown (*Cavendish Laboratory, Madingley Road, Cambridge, UK*). If I understand it right, the dilution effects that you are describing will not affect thermodynamically stable particles. For example, are metal wear particles from the engine unaffected by dilution?

N. Collings. All particles, whether vapour or solid, are subject to growth (due to condensation, agglomeration, etc.) during the dilution process, so the 'stable' particle spectrum will still be a strong function of dilution conditions, whatever form they originate in.