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39

# Formation and growth of nanoparticles as a result of the ambient dilution process

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## Introduction

The problem of the generation, growth and measurement of nanoparticles in the immediate vicinity of the vehicle exhaust is currently of great interest in the study and improvement of urban air quality. Nanoparticles are of interest for two reasons. Epidemiological studies suggest a link between atmospheric particle concentrations and health effects [6]. Experiments on rats have shown that the lung retention of nanoparticles is more significant than that of coarser particles causing a more significant toxic response even when the particles are inert [1].

Dilution causes the nucleation of gas phase particle precursors which change state from the gas phase to form nanoparticles. Up to 90% of the number of particles emitted by a vehicle maybe formed during dilution of the exhaust gas. It is therefore the particle distribution in dilute exhaust that is of interest. The mass of nanoparticles is too small for them to be accounted for reliably by gravimetric analysis and as health effects have been linked with the number of nanoparticles current researchers consider the number weighted size distribution of particles. The Scanning Mobility Particle Sizer is the most popular instrument currently used to measure the particle size distribution in dilute exhaust.

Currently there are many different types of dilution tunnel being used by researchers who are investigating nanoparticle emissions from internal combustion engines (2,3,5,7,10). There is some uncertainty as to what extent the difference in dilution tunnels may affect the results from different researchers and how closely the tunnels represent ambient dilution. There are a number of dilution parameters which vary from one dilution tunnel to another and may be responsible for transforming the particle size distribution measured after dilution. These parameters include the volume dilution ratio (ratio of dilution air to exhaust gas entering the tunnel), the dilution air temperature and relative humidity, the dilution rate (how the concentration of exhaust gas is reduced as a function of time). The sensitivity of particle distribution to dilution air temperature and relative humidity has been demonstrated (3,10) and there are good physical reasons supporting the observed results. However while it has been observed that changes in the geometry of dilution tunnels and associated changes in dilution rate have effects (3,12) there has not been a study to characterise the link between these dilution parameters and the measured particle size distribution. Establishing this characterisation constitutes the first aim of this work and involves a study of the fluid mechanics of dilution. A theoretical investigation of the mechanics of dilution gives an insight in to how turbulence characteristics may affect particle nucleation.

The temperature of the raw exhaust gas immediately before dilution is shown to significantly affect dilution induced particle nucleation. Reducing the raw exhaust temperature is found to be a simple method of reducing the number of particles emitted by a vehicle and may also be a simple metric for evaluating the emission of nanoparticles of a vehicle. A critical temperature exists where gas phase particle precursors will condense and if they are condensed in the exhaust pipe then they will not be free to nucleate during dilution.

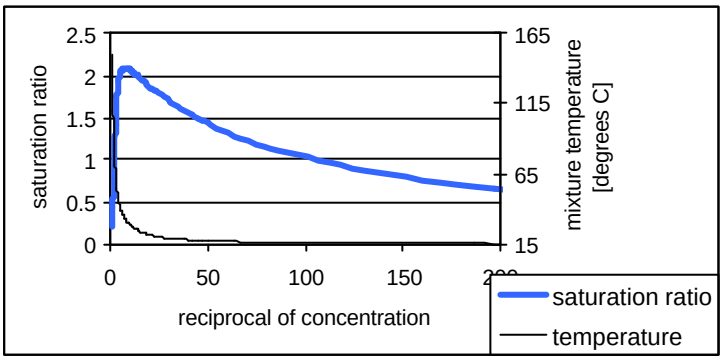
## Dilution Induced Particle Nucleation (Brief Description)

Nucleation of particles during dilution is the change of state of some molecules from the gas phase to the liquid or solid phase. The change of state occurs because the dilution causes changes of the temperature and concentration of the gas phase molecules, which we will refer to as particle precursors. Condensation and nucleation of gas phase particle precursors depends on the saturation ratio with a high saturation ratio indicating more chance of a change of state. The conditions that promote a high saturation ratio are low temperature in conjunction with high concentration where saturation ratio is defined as

$$\text{saturation ratio} = \frac{\text{partial pressure}}{\text{saturation vapour pressure}}$$

Partial pressure is proportional to concentration and the saturation vapour pressure is a function of temperature, reducing as temperature reduces. When the saturation ratio exceeds one then if there is available surface material such as other particles condensation happens and when it exceeds another critical value greater than one nucleation of new particles occurs. The following graph shows the saturation ratio and mixture temperature for water vapour at 160C as it dilutes into air at 15C.

**Figure 1 Dilution of water vapour in air**




As dilution takes place the saturation ratio passes through a peak as can be seen with this example of water vapour. This dilution induced peak in saturation ratio is similar for exhaust gas particle precursors. Any dilution induced condensation or particle nucleation will occur during this peak and once the peak has passed no more particles will be formed and relative to the dilution time scale the particle distribution will be stable. For exhaust this critical dilution ratio where the particle distribution is stable depends on the concentrations and chemical composition of the gas phase particle precursors. Due to the diverse nature of exhaust gas particle precursors putting an exact value to the critical dilution ratio is not possible. However during dilution the mixture temperature asymptotically approaches the ambient temperature and so the saturation vapour pressure also tends towards a minimum. Therefore further dilution can only cause a reduction in saturation ratio and so the critical dilution ratio is certain to be reached by the time the mixture temperature approaches the ambient temperature.

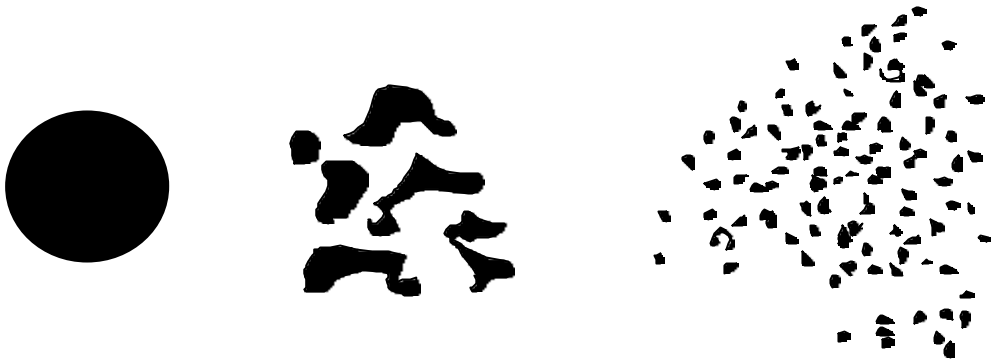
In terms of dilution tunnel design, the volume dilution ratio should exceed the critical dilution ratio otherwise the measured particle distribution may be sensitive to small changes in the volume dilution ratio. During ambient dilution the process is not halted at a particular dilution ratio where some gases may be critically saturated and this is likely to be happening in CVS dilution tunnels especially at high load conditions where volume dilution ratios can be as low as 4 to 1 [5].

The nucleation and coagulation of particles takes a finite time described by rate constants and so to investigate the effect of varying turbulence during dilution on particle formation we need to look at the quantity of particle precursor that saturates, the degree of saturation but also the time period for which it is saturated. To do this a more detailed focus on the dilution process is necessary.

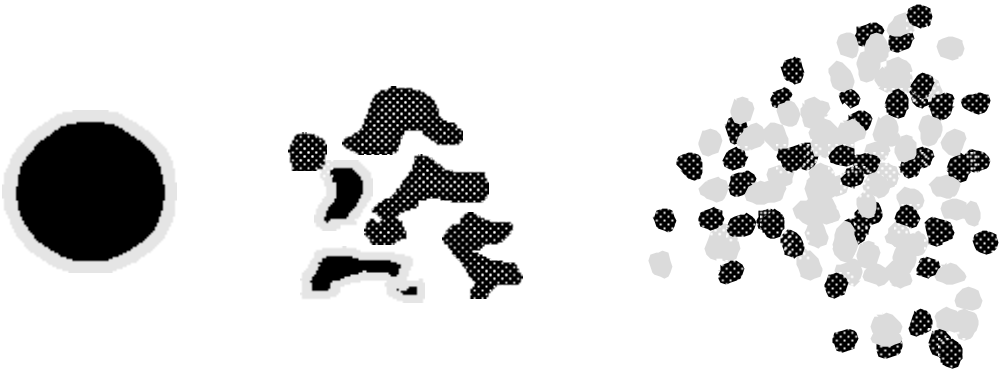
## Dilution process

Dilution of two gases is effected by turbulent and diffusive mixing. Turbulence causes the break up of the exhaust jet down to the smallest scale of turbulence, the Kolmogorov scale. Diffusion causes the mixing of the two gases on a molecular scale. Turbulence by itself will split the two gases up into small packets the size of the Kolmogorov scale but without molecular scale mass transfer such as diffusion and heat transfer these packets would remain as pure exhaust. The molecular diffusion processes are responsible for the dilution that will cause changes in partial pressure, temperature and saturation of the exhaust gas. Molecular diffusion is driven by a scalar gradient according to Ficke's law. So for example mass diffusion will occur at the interface between exhaust and air i.e. where there is a significant gradient in concentration. This means that as the turbulence breaks up the exhaust gas into smaller and smaller clumps the rate of diffusion increases correspondingly. So in effect the mixing process can be seen as being initially dominated by turbulence and then at some point becoming dominated by diffusion. This relationship between the turbulent and diffusive mixing processes is illustrated in figure 2. The grey shaded area represents the volume affected by diffusion.

**Figure 2**
Graphical representation of turbulent mixing of an exhaust clump



Graphical representation of turbulent and diffusive mixing of an exhaust clump



## Dilution Model

The dilution process is modeled using a direct numerical simulation of a decaying turbulent flow. The velocity field is used to feed the scalar transport equation which enables solution of the spatial and temporal concentration field in a turbulent flow.

As the DNS equations explain all of the physical fluid dynamics of the turbulent flow the equations must be resolved down to the Kolmogorov scale to ensure accurate results. This limits the maximum dimension of the domain as with many computations to complete on each time step only a limited number of grid points can be resolved over in a realistic time period. This has put a barrier in the way of DNS being using to solve experimental scale turbulence problems.

However for this case of a quantity of exhaust gas mixing in air the DNS results can be used to give useful information with regard to a full scale problem. The size of an exhaust clump leaving a vehicle exhaust is of the order 0.03m and the maximum size of a clump that can be modeled by the DNS is 0.001m. However we know the time scale for the turbulence to split the gas from a clump of size 0.03m to a clump of size 0.001m and we know that the rate of diffusion of a clump is dependent on the size of the clump. If we

compare the time scale of dilution with the clump size we find that negligible diffusion has taken place by the time we have reached a scale that is evaluable by the DNS.

The DNS solves the momentum equation, continuity equation and scalar transport equation which in non dimensional form are

$$\frac{\partial u}{\partial t} + u \cdot \nabla u = -\nabla p + \frac{1}{\mathrm{Re}} \Delta u \qquad \text{momentum equation}$$

$$\nabla \cdot u = 0 \qquad \text{continuity equation}$$

$$\frac{\partial f}{\partial t} + u \cdot \nabla f = \frac{1}{\mathrm{Re}\, Sc} \Delta f \qquad \text{scalar transport equation}$$

Where Re refers to Reynolds number and Sc to Schmidt number, u is the vector of velocity and p is the pressure scalar and $\phi$ is the transported scalar such as temperature or concentration.

The pressure term is removed from the momentum equation by taking the divergence of the momentum equation and then using the continuity equation an expression for pressure is obtained which can be substituted back into the momentum equation. That leaves the modified momentum equation and the scalar transport equation as the two equations to be solved. These non linear differential equations are solved using spectral methods where the physical space variables such as velocity vectors and scalars are represented by Fourier transforms. The differential of a variable with respect to x is given by multiplying the variable by the x component of the wave number. Both equations have an advection term which is non linear and a diffusion term which is linear. Both the linear and non linear terms are formed in Fourier space as products of wave number and velocity. However when multiplying two Fourier space dependant variables in the non linear terms the operation is done in physical space to avoid the complex convolution terms that would arise in Fourier space. A fast Fourier transform is used to effect the regular transfer of the dependant variables back and forth from physical space to Fourier space. The linear and non linear terms are then advanced using a semi-implicit Runge Kutta time stepping scheme.

## Model results

The main result from the model presented here is a test case for water vapour diluting into air. A clump of water vapour is at 250C and dilutes into air at 0C. The model can be run with no turbulence which gives something like the slowest possible dilution you could expect or with a high initial turbulence intensity which in this case is eddies of length scale 1mm and velocity scale 0.15m/s. Figure 3 shows the percentage of the diluting gases that is saturated as a function of time for the simple diffusion case and for the case with a significant initial turbulence intensity. The amount of gas saturated and the degree of saturation are shown as being the same for both cases, the effect of the turbulence is to accelerate the dilution process and as such reduce the time that the gases are saturated. Figure 4 shows how the turbulence decays with time including the integral

length scale, Kolmogorov scale and turbulence intensity plotted against time. The turbulence characteristics indicate why the time for dilution only changes by a small factor following a significant change in the initial turbulence intensity. As the turbulence decays the Kolmogorov scale increases and in fact it increases to a size where diffusion becomes relatively slow before the clump of gas has been broken down to the Kolmogorov scale by the turbulence.

**Figure 3 Saturation of diluting water vapour, DNS predictions**

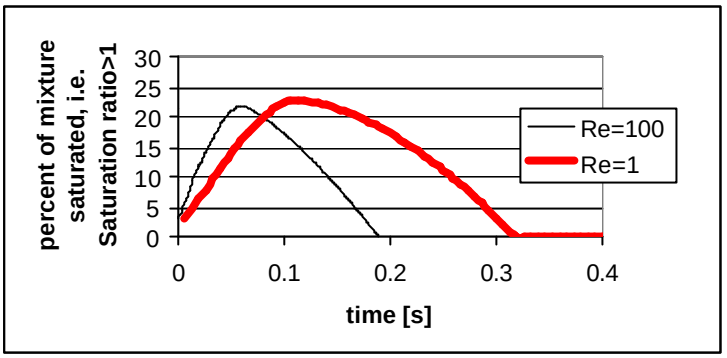
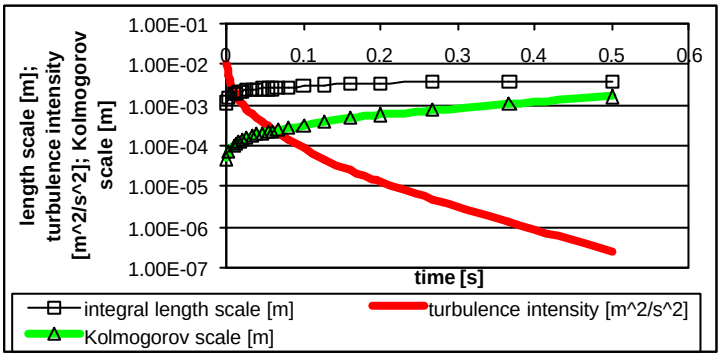



**Figure 4 DNS turbulence characteristics for Re=100**

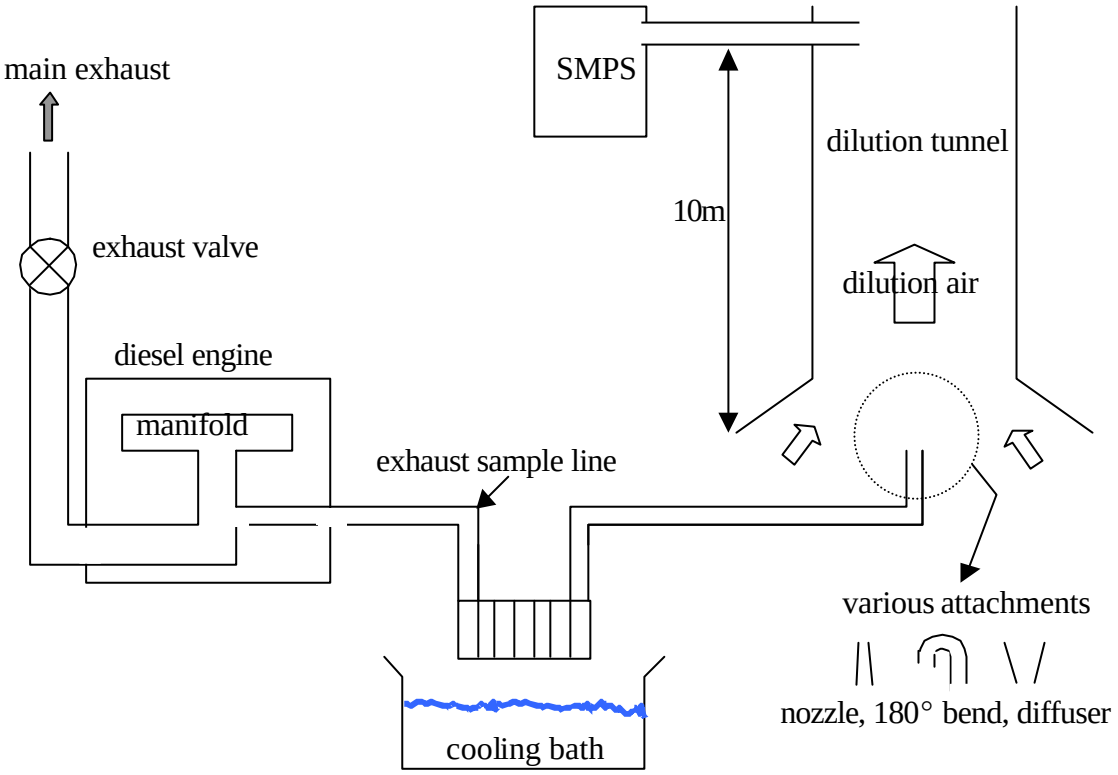



For sustained turbulence where the Kolmogorov scale remains constant as would be found in an ejector pump style dilution system where the turbulent energy is maintained by a compressed air supply. Here dilution happens much quicker than the decaying turbulence case. The Kolmogorov scale is sustained at around $1x10^{-5}$m as opposed to raising up towards $1x10^{-3}$m very quickly. At a scale of $1x10^{-5}$m the exhaust gas is diluted by diffusion extremely quickly by comparison to the eddy turn over time. This means that in one eddy turn over time the gas will be completely diluted. A typical eddy turn over time based on the dimensions and flow rates in an ejector pump would be of the order of 1ms.

## Experimental Results

A direct injection 2.5litre diesel engine was used as the particle source. The main exhaust flow leaves the laboratory via a ventilation duct. A sample of the exhaust is tapped from the engine exhaust manifold for dilution. A valve in the main exhaust line makes it possible to slightly increase the pressure in the exhaust manifold and thus control the flow of exhaust gas to the dilution tunnel. The dilution tunnel is a ventilation duct of square cross section with 0.4m sides and a mean flow velocity of 3 to 4 m/s. The Kolmogorov scale in the duct is estimated to be greater than 1mm. This indicates a low level of sustained turbulence intensity in the dilution tunnel. The engine is run at steady state for all experiments and is run for half an hour before experiments begin.

**Figure 5 Diagram of Apparatus**

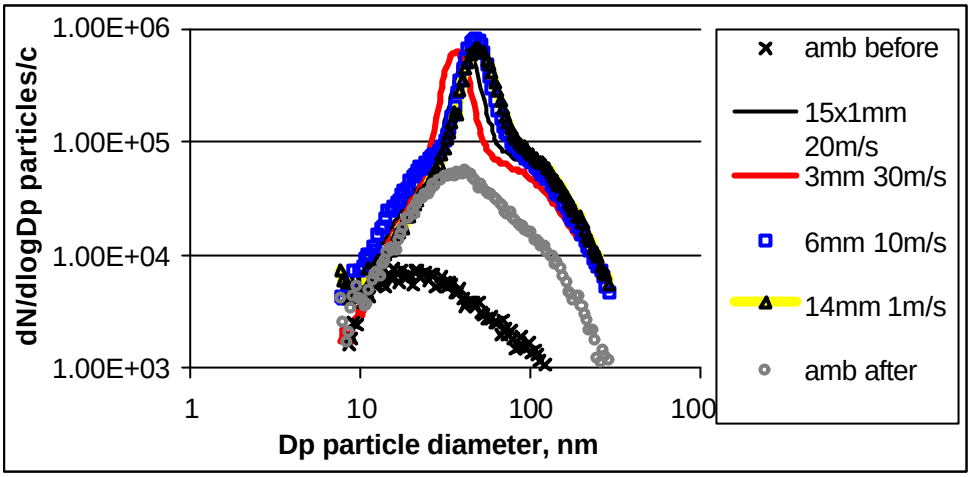



Variable sample flow velocity

The idea of this experiment is to change the flow velocity of the exhaust sample as it enters the dilution tunnel thus changing the initial turbulence intensity. Various sample pipe outlet diameters are tested with the flow velocity varying from 1m/s to 30m/s. Small differences in the measured particle distribution are observed as the flow velocity is changed (figure 5). The trend is that as the velocity increases the magnitude of the particle number concentration falls a little bit across the size range. The hypothesis to

explain this effect is that as the sample outlet cross section reduces the flow in the sample line reduces slightly thus effectively increasing the ratio of air to exhaust in the dilution tunnel.

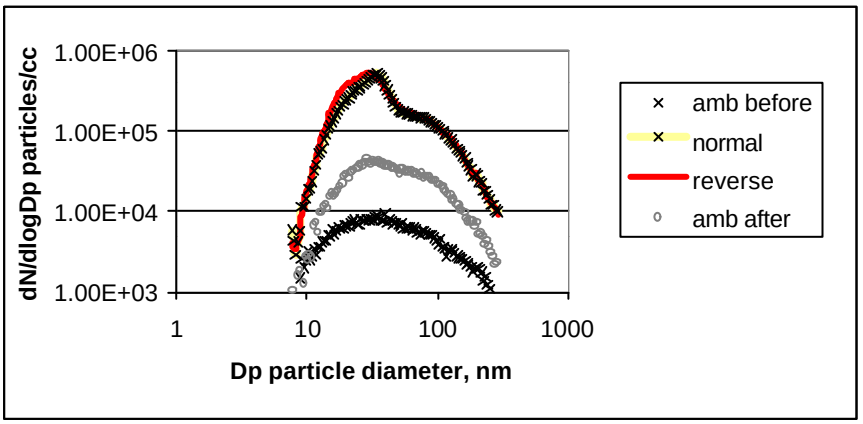
**Figure 6 Effect of exhaust outlet velocity**




<u>180 degree bend</u>

When the standard sample line was compared with the 180 degree bend again there was no significant difference in the measured particle size distribution (figure 7). It can be seen that the ambient level measured after the experiment was notably higher than the level measured before the experiment but that once the engine is turned off the ambient level starts to fall again.

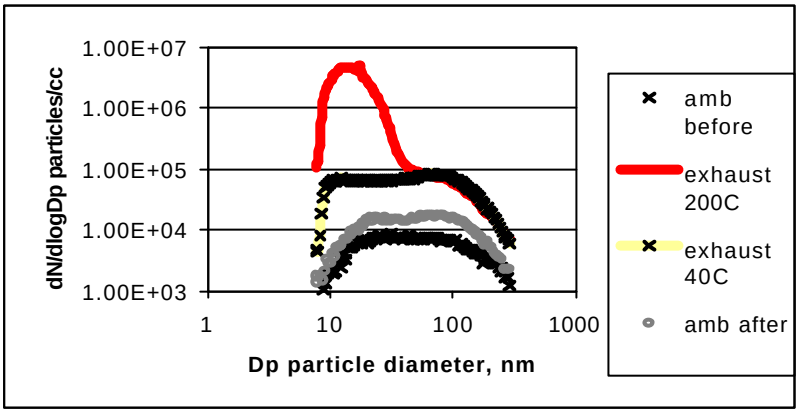
**Figure 7 Effect of exhaust outlet orientation**



Raw exhaust temperature

Using the standard sample line but cooling the exhaust gas by immersing the sample line in cold water gave an investigation of the effect of varying the raw exhaust gas temperature. A change in exhaust temperature from 200C to 40C gave a significant reduction in the number of nuclei mode particles that are forming during dilution (figure 8). The hypothesis put forward for this result is that the reduction in raw exhaust temperature invokes the condensation of gas phase particle precursors onto existing surfaces in the sample pipe such as the internal walls of the pipe or accumulation mode particles. Then during dilution the concentration of gas phase precursors is much lower than in the high temperature case where they are able to pass through the pipe without condensing. This would explain the significant reduction in nuclei mode particles.

**Figure 8 Effect of raw exhaust temperature**




## Implication of results

Turbulence intensity: Theoretical predictions of the saturation of water vapour in decaying turbulence show that varying the initial turbulence intensity can change the time that the water vapour is saturated by less than a factor of 2 with the time being of the order of 0.5s. However when comparing this with sustained turbulence the time that the steam is saturated is reduced by 1 or 2 orders of magnitude. This suggests that for decaying turbulence the dilution is slow with respect to the time scales needed for the nucleation of particles and that a change in the initial turbulence intensity does not significantly affect the time scale for dilution. This would explain why the particle distribution was shown to be not sensitive to changes in the exhaust sample flow velocity or orientation. These changes in the sample pipe outlet affect the initial turbulence intensity but the dilution is effectively happening in decaying turbulence and so they have little affect on the time scale for dilution. However the time scale for dilution in sustained turbulence of an intensity similar to that found in ejector pumps is much shorter than for decaying turbulence. This might explain why significant sensitivity to dilution rate has been noted when diluting with ejector pumps.

As a first attempt at characterising dilution tunnels the theory and experiments suggest that a key factor is if the turbulence intensity in the tunnel is sustained at a high level or not. If the base level turbulence intensity is negligible with respect to the turbulence caused by the exhaust issuing into the tunnel, as is the case in the atmosphere, then the particle distribution in the dilution tunnel will be representative of real world dilution. As long as the turbulence is decaying the initial turbulence intensity is not a variable that significantly affects particle size distribution.

Raw exhaust temperature: The variable that has the most significant effect on particle size distribution is the temperature of the raw exhaust gas before dilution takes place. This parameter should be considered before any particle measurements can be compared. The length of a sample pipe or amount of insulation could change the raw exhaust temperature and potentially change the measured particle size distribution completely. The gas phase particle precursors contained in exhaust are many and diverse and vary from engine to engine and this makes it difficult to evaluate a particle forming potential of vehicle exhaust based on the composition of the exhaust gases. However by definition all the gas phase particle precursors will condense or nucleate by the time they reach ambient temperature, as otherwise they are not particle precursors. This means if the raw exhaust is cooled to ambient temperature then there will be no new particle formation during dilution. Instead all the gas phase particle precursors will condense on to the coarser particles and surfaces in the exhaust and even if there is some nucleation, coagulation in the raw exhaust is too fast to allow a notable increase in particle number. Therefore the exhaust temperature which is a simple parameter to control and even simpler one to measure is a clear indicator of the particle forming potential. As the majority of particles 90% (effectively the entire nuclei mode peak) are formed during dilution then setting a maximum exhaust temperature would be an effective way of limiting the number of particles emitted by vehicles. For the diesel engine used in this experiment then if the raw exhaust gas is dropped to 40C before dilution then the nuclei mode is removed, however as the experimental setup did not have the capability to cool the exhaust in say 10 degree intervals the actual temperature needed is not known and maybe higher than 40C. It would be simple to repeat this experiment for numerous vehicle exhausts and find out the temperature needed at different load/speed conditions for each engine. It would then be possible to do on road tests and measure the actual exhaust exit temperature under driving conditions and from this work out the specifications for an exhaust to air heat exchanger that would guarantee to eliminate dilution induced particle nucleation.

## Conclusions

Dilution in sustained turbulence found in ejector pumps is much faster than in decaying turbulence found in the atmosphere.

DNS predictions show the time history of the saturation ratio of particle precursors during dilution in decaying turbulence. The results are found to be only weakly affected by changes in the initial turbulence intensity.

Experiments indicate that when diluting in decaying turbulence particle size distribution was not sensitive to changes in initial turbulence intensity.

Experiments showed that particle size distribution is significantly sensitive to the temperature of the raw exhaust gas at entry to the dilution tunnel.

## Acknowledgements

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## References:

1. Donaldson,K., Li,X.Y. and MacNee,W. (1998) "Ultrafine (nanometre) Particle Mediated Lung Injury", J. Aerosol Sci. Vol 29 Number 5/6, pp. 553-560

2. Greenwood,S.J., Coxon,J.E., Biddulph,T. and Bennett,J. (1996) "An Investigation to Determine the Exhaust Particulate Size Distribution for Diesel, Petrol and Compressed Natural Gas Fuelled Vehicles", SAE paper number 961085

3. Kittelson,D.B. and Abdul-Khalek,I.S.(1998), "Nanoparticle Formation during Exhaust Dilution", 2nd ETH workshop on Nanoparticle Measurement, Zurich

4. Lesniewski,T. and Friedlander,S.K. (1995) "The Effect of Turbulence on Rates of Particle Formation by Homogeneous Nucleation", Journal of Aerosol Science and Technology Vol 23 pp. 174-182

5. Maricq,M.M., Podsiadlik,D.H. and Chase,R.E. (1999) "Examination of the size-resolved and transient nature of motor vehicle particle emissions" J. Environmental Science and Technology, Vol 33, n 10, pp 1618-1626

6. McAughey,J.J. (1997) "Regional Lung Deposition and Dose of Ambient Particulate in Humans by Particle Mass and Number", Research report AEA Tech. Aerosol Science Centre, Oxfordshire UK

7. Rickeard,D.J., Bateman,J.R and Yeong,K.K. (1996) "Exhaust Particulate Size Distribution : Vehicle and Fuel Additives in Light Duty Vehicles", SAE paper number 961980

8. Sander,U.H.F., Fischer,H., Rothe,U. and Kola,R. (1984) "*Sulphur, Sulphur Dioxide and Sulphuric Acid*" The British Sulphur Coorporation

9. Seinfeld,J.H. (1986) "*Atmospheric Chemistry and Physics of Air Pollution*" Wiley

10. Shi,J.P. and Harrison,R.M. (1999) "Investigation of ultrafine particle formation during diesel exhaust dilution" J. Environmental Science and Technology, v 33, n 21, p 3730-3736

11. United Kingdom Quality of Urban Air Review Group, (1996) "Airborne Particulate Matter in The United Kingdom" Third Status Report

12. Wei,Q., Kittelson,D.B. and Winthrop,F. (2001) "Single Stage Dilution Tunnel Design", SAE paper number 2001-01-0207