URGENT Project

EVOLUTION OF THE PARTICLE SIZE DISTRIBUTION OF VEHICULAR EMISSIONS IN THE URBAN ATMOSPHERE

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Lead Researcher: Dr A G Clarke, Leeds University
Tel: 0113 2332510, Fax: 0113 2440572, e-mail: a.g.clarke@leeds.ac.uk

P.I. at Middlesex University: Prof. R.S.Hamilton
Tel 0181 3626638 Fax 0181 3625232 e-mail: R.Hamilton@mdx.ac..uk

Associate Researchers:
Dr B Gorbunov, Middlesex University; Dr L.A.Robertson, Leeds University

Overall Project Summary

The project focussed on the processes affecting particulates in an urban area with special reference to vehicle-derived particles. Several detailed studies were carried out as described in the following paragraphs taken from the final report (June 2001). These were carried out in parallel with the development of a trajectory model of the evolution of the particle size distribution of vehicular emissions across an urban area. A technical description of the model is given below.

1. **Coagulation** M*ethods for modelling coagulation* (Ref.4) of non-spherical aerosol particles, soot in particular, have been reviewed and the major uncertainties associated with the fractal dimension have been identified. It was shown that coagulation coefficients for non-spherical particles could differ considerably from those obtained for spherical model particles. Three different computer codes for calculation of the aerosol size distribution evolution due to coagulation, nucleation, evaporation/condensation and sedimentation have been developed and verified. The codes were prepared on a Windows platform to be incorporated later into a Lagrangian aerosol evolution model as a coagulation module. The codes enable coagulation of non-spherical aerosol particles with known fractal dimension to be modelled. The best performance was obtained for a code based upon the Monte Carlo technique of direct simulation of collisions of aerosol particles from different size classes.

Fractal dimension of soot aggregates. (Refs. 1,6) A novel integrating method has been suggested for the calculation of the fractal dimension of soot aggregates based on the approximation of a constant fractal dimension in the size range of the interest. The new approach enables the link between the mass of a particle and the mobility radius to be expressed with a simple formula and the parameters to be determined from experimental data. The approach has been tested on aerosol size distributions obtained by Ford Research Centre in Aachen (Germany). Collaboration with this centre was established. A diesel exhaust sample was diluted approximately 14 fold in a bag and aerosol size distributions were measured every 5 min with a TSI SMPS system. It was found that the fractal dimension does not depend on time during the first 80 min of coagulation. The average values for this period for the fractal dimension were found: 1.92 + 0.08.

The accuracy of conventional coagulation theory (Ref.6). Calculations of aerosol size distributions with the newly developed code has been carried out and compared with the Ford data. It was found that calculated size distributions are transformed more slowly than measured ones. Thus, a conventional coagulation kernel cannot be used to describe the coagulation of soot particles. This comparison makes it possible to remove the major uncertainties with the coagulation coefficients for soot particles emitted by a diesel engine. It was shown that the coagulation coefficient in the size range from 50 to 250 nm (mobility radius) have to be increased by a factor of 1.87 to give coagulation rate compatible with experimental measurements.
Coagulation of multi-modal urban aerosol has been modelled with nucleation and water condensation/evaporation. It was found that evolution of different modes of the urban aerosol was different. The total mass as well as the size distribution of the coarse mode were unchanged during 3 hours. Therefore, the coarse mode was not involved in interaction with aerosol particles from other modes due to the low particle number concentration. There were found to be only slight changes in the accumulation mode peak radius (dry) and the total dry mass during coagulation. This indicates that the accumulation mode under typical urban conditions is either derived from the regional background or formed as a result of urban emissions and it grows primarily due to emitted particles rather than coagulation with the nucleation mode. In a humid atmosphere, the size of accumulation mode particles is influenced by humidity due to water uptake. Although freshly emitted soot particles are hydrophobic a relatively small increase in their dry mass due to the coagulation with hydrophilic nucleation particles can affect water uptake and the size/mass of these particles in the humid atmosphere.
The most pronounced effect of Brownian coagulation was found for the nucleation mode. There are two main features of the evolution of the nucleation mode due to coagulation:

- Self-coagulation of aerosol particles belonging to the nucleation mode;
- Inter-mode coagulation of particles between the nucleation and accumulation modes.

These two types of coagulation compete to each other. The mass transfer from the nucleation mode to the accumulation mode is influenced by the mass concentration of aerosol in both modes. A simple parameterisation for the mass transfer was obtained from the modelling results:

2. Nucleation (Refs. 3,7) Nucleation is relevant to this project partly because of particle formation processes in the diluting exhaust (organics and/or sulphuric acid) and partly because the ultra-fine mode in the atmosphere will have a major contribution from gas-to-particle processes related to atmospheric chemistry as well as a contribution from vehicular exhausts. A new realistic theory of the atmospheric aerosol formation in a multi-component atmosphere has been developed. Multicomponent homogeneous nucleation is considered in the case of dominant and trace species (in the respect of embryo composition). The free energy of embryo formation for multi-component homogeneous nucleation has been derived for systems with several dominant species, e.g. water + sulphuric acid and a number of trace substances: eg. nitric acid, organic acids, ammonia. This treatment is based on a differential version of the capillarity approximation. It was found that the free energy of embryo formation for multi-component nucleation depends upon the ratios of the partial pressures of the trace species to the Henry's law constants of the species. The

nucleation rate for a multi-component system is found to be a product of the dominant species nucleation rate (e.g. binary or ternary nucleation rate) and the correction factor that is influenced by the trace species. It was shown that the multi-component correction factor is likely to be in the range from 3 to 10^{10}.

3. Evaporation/Condensation of Organics A significant fraction of vehicular exhaust particulates consists of organic material with a wide range of molecular weights and volatilities. Evaporation and condensation processes take place both in the exhaust system, during rapid dilution in the vehicle wake and in the general atmosphere. The significance of these processes for the particulate mass and size after discharge into the atmosphere is very poorly quantified and was therefore a focus for detailed analysis in this project. The theory for multi-component evaporation/condensation of organics is fairly well established in situations where the surface-to-gas transfer processes are rate determining. A computer program was written to estimate these rates and physical data compiled or estimated for typical species including C-16 to C-28 straight chain alkanes, C-16 to C-19 straight chain acids, a representative selection of PAH, plus a small number of other species such as cresols and benzoic acid. However it became clear from our own work and that of others that in most situations the intra-particle diffusion process is rate determining. The appropriate diffusion coefficients are not available and the best formulation of the radial diffusion problem is subject to debate in the literature. The decision was taken that this aerosol process was too complex to be incorporated into the trajectory model at this stage. However a presentation on some of the results relating to gas phase versus intra-particle diffusion was made at the European Aerosol Conference 2000 (Ref. 5).

References

Extended abstracts based on presentations or posters at the European Aerosol Conferences 1999 and 2000.

1. B. Gorbunov B., A.G. Clarke and R.S. Hamilton (1999) Coagulation of soot particles and fractal dimension. J. Aerosol Sci., 30, Suppl. 1, pp. S445-6.
2. B. Gorbunov , M. Moore, I. Williams and R. Hamilton (1999) The relationships between PM10, PM2.5 and other pollutants in an urban area (Lagrangian model and experiment). J. Aerosol Sci., 30, Suppl. 1, S409-10.
3. B. Gorbunov B. (1999) Heterogeneous multi-component nucleation in a system with a dominant species. J. Aerosol Sci., 30, Suppl. 1, pp. S67-8.
4. B. Gorbunov, A.G. Clarke and R.S. Hamilton (2000) Modelling coagulation of soot particles. J. Aerosol Sci., 31, Suppl. 1, pp. S811-2.
5. L.A. Robertson and A.G. Clarke (2000) Semi-volatile organic aerosols - assessment of gaseous and intraparticle diffusion processes. J.Aerosol Sci., 31, Suppl. 1, pp. S94-95.

Papers in refereed journals:

6. B. Gorbunov, V. Scheer, A.G. Clarke and R.S. Hamilton, Coagulation Of Soot Particles And Fractal Dimension (2001) J. Aerosol Sci. Under review.
7. B. Gorbunov, From Binary to Multi-component Nucleation - Atmospheric Aerosol Formation. J. Chem. Phys. 115,2641-2651 (2001).

Conference Presentation Pending
Seventh International Highway and Urban Pollution Symposium, Barcelona, May 2002. A Lagrangian Model of the Evolution of the Particulate Size Distribution of Vehicular Emissions within London. Andrew G. Clarke, Leonie A. Robertson, Ron S. Hamilton and Boris Gorbunov.

Leeds 'TRAJECTORY' Model – Technical Description

Objectives

Available models for dispersion and transport of pollutants in urban areas (such as ADMS Urban) cannot adequately take into account particle size distributions and the size dependence of aerosol processes. Lagrangian trajectory models do not have this limitation and therefore a prime objective of this project was to develop such a model which could be applied to the evolution of vehicular particulates emitted into a pre-existing background aerosol. No attempt has been made to model street canyon situations or the first few seconds of dilution in the vehicle wake. Rather, the approach addresses such questions as "what peak particle number concentration may be reached in the city air away from the roadside?" , "what changes take place in the transport of city centre vehicular emissions to the suburbs?" or "how persistent is the ultra-fine mode downwind of the emissions?".

A completely new computer program based on a trajectory model has been developed and is being applied to London. . It provides a platform from which to study the combined effects of emissions, dispersion and transport, dry and wet deposition, coagulation,etc, as an air parcel moves across the city. It explicitly allows for the effects of particle size on all the processes. Output files give the particle mass (as PM10, PM2.5, PM1 and PM0.1) at each point along the trajectory and the particle number in each size fraction.

Work is currently under way to identify the effect of the individual aerosol processes on the observed size distributions and mass concentrations and to compare the predicted results with data obtained in London for PM10 and PM2.5 (TEOM data) and particle size obtained by the DETR funded monitoring project using SMPS instruments. These results are to be presented at the Highways Symposium in Barcelona, May 2002 and subsequently published.

Emissions

The emissions data are drawn from the published inventory for London giving annual mass emissions on a 1km grid square basis. Two categories of emissions - 'vehicular' and 'other' are considered separately. All emissions are assumed to be at ground level. Vehicle emissions are adjusted for time of day, day of week, month of year. Time of day factors allow for central, inner and outer London cordons. Since trajectories extend over several hours the vehicular emissions factors vary with actual time of day during the run. 'Other' emissions are assumed to remain constant with time.

Size Distributions

The size range covered is usually taken to be 10 nm to 10000nm diameter(10μm) and is subdivided into (typically) 30 bands defined logarithmically (dlogd=0.1). Emissions and initial size distributions are take to be the sum of 3 log-normal distributions each described by a geometric mean diameter D_g and σ_g . The first mode represents ultrafine particles typical of vehicular emissions. The second is for accummulation mode particles. The third is for coarse mode particles. The vehicular, 'other', and background aerosols can be represented as a single mode or a mixture defined on a mass % basis. (See setup data sheet below). The coarse mode can be introduced as an additional percentage of the vehicular emissions to represent re-suspended road dust and/or be included in the background and 'other' emissions'. Mass concentration or emission values are converted to the corresponding number of particles. The log-normal distributions are truncated at the size limits (usually 10nm and 10000nm) and the numbers scaled up to correct for particles which a log-normal distribution would place outside the limits so that the right mass to number conversion is achieved.

Vertical Structure

A 4 layer structure is assumed. The lowest, surface layer is usually taken as 50m**,** followed by a canopy layer (eg. 100m thick). The third layer stretches to the top of the boundary layer which is variable in height as determined from the meteorology. The boundary layer is allowed to drop to 50m thereby potentially eliminating layers 2 and 3 and in these circumstances the particles within them disappear into the reservoir layer above. In situations of a rising boundary layer, reservoir air with a defined mass concentration is drawn in and layers 2 and 3 can be re-established. Concentrations within each layer are assumed uniform.

The vertical dispersion is described by a simple transfer term between layers based on the eddy diffusivity at the height of the layer interface and the concentration gradient estimated from the difference in concentration of the adjacent layers. and the interlayer spacing.

Meteorology

Hourly met data is drawn from the Met. Office via BADC for one of the London sites (eg London Airport). This is then edited to exclude unwanted data and pre-processed to produce the necessary parameters for dispersion calculation. These include the boundary layer thickness, friction velocity, Monin-Obukov length, etc. These hourly data are linearly interpolated to the actual time of day in the trajectory. (MO length is interpolated on an inverse basis since it could go to infinity).

Trajectories

As the program is currently written the trajectories are either assumed to be linear or can follow the prevailing 10m wind direction. Use of a numerically defined wind flow field from separate calculations could be envisaged in the future. The starting point for any trajectory is specified in terms of the ordnance survey grid co-ordinates at an upwind point on or near the limit of the emissions inventory area. When linear trajectories are assumed it is possible to ensure that the trajectory passes over a particular receptor.

Background Aerosol
The background PM10 mass concentration must be defined. This could come from a wider area model (eg. using Met. Office NAME model) or on the basis of experimental data at rural sites adjacent to the city under study. For London the only relevant rural PM10 sites are Rochester and Harwell. The background aerosol in layers 2, 3 and the reservoir will generally not be know and the program allows these to be defined as a % of the ground level background (eg. 100%, 80%, 50%) (see Setup data sheet).

Aerosol Processes
Background concentrations and emissions have been covered above.
Dry deposition is particle size dependent and is described by a combination of sedimentation, and a deposition including an aerodynamic resistance (defined by the meteorology) and the laminar sub-layer resistance. Sedimentation of coarse particles is allowed to contribute to transfer between layers 3 to 2 and 2 to 1.
Wet deposition is particle size dependent and increases with precipitation intensity which must be user supplier.
Coagulation is described using conventional theory except that when particles collide the size of the aggregated particle is estimated using a user-defined fractal dimension rather than FD=3 (liquid drop model). Since coagulation only affects ultrafine particles significantly, a value FD=2, typical of diesel particles is more appropriate. Coagulation is only included in the surface layer closest to the emissions.

Other processes,including the effects of humidity on deliquescent particles could be added at a later date.

Computation, Input and Output
The input data required are mostly held in files:
Hourly met.data file.
Emissions inventory file
Time of day/day of week/month of year correction factors file
Scavenging coefficients as a function of particle size
Setup file of various parameters.
A few parameters are input from the terminal at run time.

After setting up the initial conditions the trajectory is evolved with a time step of 30-60s. The concentrations are solved using a linear approximation
c(time n+1)=c(n) + dt*[dc(time n)/dt] .
Improved numerical schemes could easily be incorporated but results showed virtually no change in output (maximum change along trajectory of 0.1ug/m^3) for change in time step to 10s or 90s.

The output is directed to two files. One has time/location and mass concentration data for each layer at the end of each step (PM10, PM2.5, PM1.0, PM0.1). The other has the particle numbers in each size band at each step. No graphical processing of the data is incorporated into the programme but the files can be read into EXCEL or other packages for processing. For example the number data can be plotted as number size distributions on a log-log scale or converted to mass distributions and then plotted.

A Typical Setup File

Particle Charactistics

Lowest Diameter (nm)	Highest Diameter (nm)	No of Intervals	Fractal Dimension
10	10000	30	2

Log-Normal Modes (1 - ultrafine, 2 - accum.n, 3 - coarse)

Mode No	Density (g/cm3)	Diameter Dpg (nm)	Sigma
1	2	75	1.5
2	2	500	1.8
3	3	4000	1.8

Emissions - Percent in each mode based on inventory mass values
(Not restricted to total 100%)

	Mode 1	Mode 2	Mode 3
Background	0	90	10
Vehicular	100	0	15
Non-vehicular	0	80	20

Initial Vertical Concentration Profile

Canopy Layer (% of background surface layer)	Upper Layer (% of background)
100	80

Vertical Structure

Surface Layer (m)	Canopy Layer Thickness (m)
50	100

Trajectory

Length (hours)	Time Step (s)
3	60

Include Coagulation(yes/no)?
yes