6.26 MODELLING THE FORMATION AND SIZE-SPECTRUM EVOLUTION OF URBAN PARTICULATE MATTER WITH FAST ALGORITHMS

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INTRODUCTION

Many air-quality models have designed and incorporated structures for handling the chemistry of particulate matter. These, in reality, are extended version of photochemical mechanisms with specific additions to olefin species to account for biogenic olefins, and a condensable organic gas species as described by Environ at CAMx (2002). In theory these are hybrids of linear aqueous sulphate chemistry and parameterized sulphate/nitrate/ammonium equilibrium in order to calculates following transformations like: SO2 to sulphate via aqueous reactions, condensable organic carbon to aerosol organic carbon, sodium nitrate formation, gaseous HNO3 to aerosol nitrate and gaseous NH3 to aerosol ammonium. However, No particle size distribution is currently directly modelled and usually this is done by semi-empirically selection a representative size range and density for each aerosol species in the chemistry parameters file.

In other type of models the size distribution is taken into account with a modal treatment of the particle size distribution. Such models has several limitations with respect to serving as the basis of a general urban/regional particulate matter modelling. First the number of modes is usually limited due to computational restriction. These modes might not sufficient for all the domain where urban aerosols modelling is required for which size distributions tend to be controlled by the local sources and meteorological conditions. Even if the total number or mass concentration obeys a log-normal size distribution, each species does not necessarily exhibit the same geometric mean diameter and standard deviation. Condensation/evaporation of a single species would change the distribution of that species over differently sized particles. Even more these models are subject to limitations of assuming that each of the two modes has the same chemical composition. In practice, however, different sized particles can have quite different chemical compositions and transport should be allowed to influence the change of geometric mean diameter and deviation since, in reality, however, turbulent mixing may bring in new particles with different statistical properties. Given the aforementioned limitations of existing approaches and taken into account the latest increases in computational potential, a full modelling approach is deemed to be more appropriate where the evolution of the particles in the size spectrum is fully considered.

THE SIZE-SPECTRUM CONSERVATION EQUATIONS

For evaluating the importance of aero-disperse particles in atmospheric processes in grid-based transport models the aerosol conservation equations must be implemented. These equations describe for the nucleation, coagulation and condensation of this particles in a certain size-spectrum. The conservation equation for the concentration of a species the gas phase S_g, is given by:

$$\frac{dS_g}{dt} = R - J n_{\hat{e}} - \sum_{i=1}^{L} C_i N_i - \ddot{e}_g^{dep} S_g - \ddot{e}_g^{dil} S_g \qquad (1)$$

Where, R is the formation rate, J the nucleation rate and N_i the concentration of aero-disperse particles containing n_i molecules of H2SO4 (κ refers to the critical cluster). L is the

total number of aero-disperse particle classes, C_i is the collision frequency between H_2SO_4 molecules and the corresponding aero-disperse particles. $\ddot{e}_g^{dep}$ and $\ddot{e}_g^{dil}$ are the corresponding deposition and dilution rates. After evaluating which particle couples ($L_{c,i}$) could coagulate to form a particle i, the conservation equations for each particle class can be expressed as the equation for aero-disperse particle dynamics:

$$n_i \frac{dN_i}{dt} = \sum_{j=1}^{L_{c,i}} (n_{j1} + n_{j2}) K_{j1,j2} N_{j1} N_{j2} - n_i N_i \sum_{l=1}^{L} K_{i,l} N_l (1 + \ddot{a}_{i,l}) + \tag{2}$$

$$+ \frac{n_i}{n_i - n_{i-1}} C_{i-1} N_{i-1} - \frac{n_i}{n_{i+1} - n_i} C_i N_i - n_i N_i \ddot{e}_i^{dep} - n_i N_i \ddot{e}_i^{dil}$$

For which, $K_{j1,j2}$ is the coagulation coefficient. For i = 1 the first term on the rhs is replaced by the nucleation term $J\, n_{\hat{e}}$ and the first condensation term doesn't exist. For the highest size class i = L the second condensation term doesn't exist. The time discretisation is carried out according to the following definitions:

$$N_i = N_i^o + f\ \ddot{A}N_i \quad and \quad \frac{dN_i}{dt} = \frac{\ddot{A}N_i}{\ddot{A}t} \tag{3}$$

Where, f is the implicitness factor <0,1>. By neglecting the non-linear and some linear terms in order to always respect the mass balance [4] the following simple system of equations will be solved for the first iteration step:

$$\frac{\ddot{A}S_g}{\ddot{A}t} = (\frac{\ddot{A}S_g}{\ddot{A}t})^o + f\ \ddot{A}R - f\ n_{\hat{e}}\ \ddot{A}J - \sum_{i=1}^{L} C_i\ \ddot{A}N_i - f\ \ddot{e}_g^{dep}\ \ddot{A}S_g - f\ \ddot{e}_g^{dil}\ \ddot{A}S_g \tag{4}$$

$$\frac{\ddot{A}N_i}{\ddot{A}t} = (\frac{\ddot{A}N_i}{\ddot{A}t})^o + f \sum_{j=1}^{L_{c,i}} K_{j1,j2} (\frac{n_{j1}}{n_i} N_{j2}^o\ \ddot{A}N_{j1} + \frac{n_{j2}}{n_i} N_{j1}^o\ \ddot{A}N_{j2}) - f\ \ddot{A}N_i \sum_{l=1}^{L} K_{i,l} N_l^o (1 + \ddot{a}_{i,l}) + \tag{5}$$

$$+ f\ \frac{(1 - \ddot{a}_{i,1})}{n_i - n_{i-1}} C_{i-1}\ \ddot{A}N_{i-1} - f\ \frac{(1 - \ddot{a}_{i,L})}{n_{i+1} - n_i} C_i\ \ddot{A}N_i - f\ \ddot{A}N_i\ \ddot{e}_i^{dep} - f\ \ddot{A}N_i\ \ddot{e}_i^{dil}$$

For more iterations, all neglected terms are taken into account with $(\ddot{A}N_i / \ddot{A}t)^o$. The above set of conservation equations are solved in a way that negative concentrations are inherently avoided. Two implicit solution schemes are incorporated in a numeric module called FIA[2]PES[2] (Skouloudis and Eifler, 1994); 1 a forward-difference and a predictor-corrector scheme. In both schemes the overall accuracy of the solutions is an input controlled parameter. Due to the specific formulation chosen the overall mass balance within the particle spectrum is always guaranteed close to the machine accuracy.

IMPLEMENTAION IN 3D MODELS

The aerosol model can be imagined as "sitting on top of" the gas-phase photochemical air quality model and the flow of information is essentially from the gas-phase model to the aerosol model. Initial and boundary particulate matter size-composition distributions are altered by the transportation over the region, modified by gas-to-particle conversion, and removed by dry and wet deposition. Gas-phase species that are involved in gas-to-particle conversion are generally end products that do not participate further in the gas-phase chemistry. Consider for example nitric acid generated by gas-phase chemistry. This, at each location and time will be partitioned between the gas and aerosol phases. That partitioning, while essential to the aerosol behaviour, does not feed back to affect the gas-phase chemistry. When droplets are present, however, the gas-phase species that can dissolve the aqueous phase include those that are intimately involved in gas-phase chemistry. The associated gas-phase air quality model supplies the flow field and turbulent dispersion algorithms as well as the local concentrations of the gas-phase species participating in gas-to-particle conversion.

Regardless of the time intervals for which modelling is to be applied, it is clear that the model must be applicable for a range of meteorological conditions e.g. periods of cloudy days, fog, windy days, drainage from the slopes, clear and cold nights, and highly stable conditions. Hence, it will be essential this module to be inherently stable for mass conservation and computationally fast.
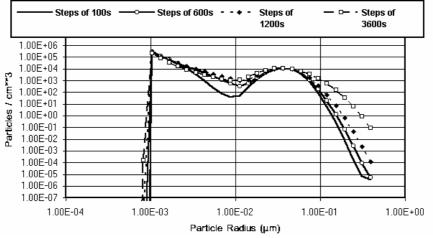

Figure 1. The aerosol-size-spectrum evolution at 7200s (const. nucl.)

A typical example of the calculations with FIA[2]PES[2] at a constant nucleation rate after 2 hours is depicted at Figure 1 by utilisation various type steps in solving the set of the equations 4-5 with 70 equidistant particle size bins. Similarly in Figure 2*Figure* are shown the total number of aerosol-particles for the corresponding time steps.
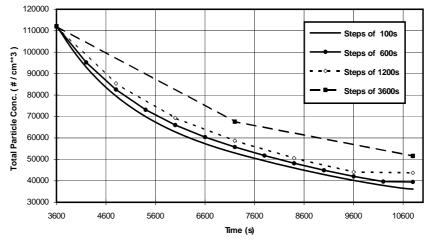

Figure 2. Evolution of total aero-disperse particle concentration (const. nucl.).

One of the important issues regarding the introduction of FIA[2]PES[2] in full-scale 3D models as CAMx is nucleation for the various species. The existence of new particle formation in the atmosphere by nucleation has been very difficult to confirm because of the absence of sufficiently small (sub - 10 nm) particle on time scales short enough to confirm a nucleation event. Candidate species that have achieved theoretical attention as nucleating agents in the atmosphere are the binary system of sulphuric acid - water and secondary organic species produced by the photo-oxidation of certain higher molecular weight precursor organics. Mathematical models of atmospheric aerosol dynamics include provision for new particle formation by nucleation through theoretical expressions for the rate of nucleation, expressed as the number of particles formed per unit volume per unit time.

For the purposes of this work, the approach of Kulmala et. al. (1998) is used. This calculates the nucleation rate and the balance term for the H_2SO_4 concentration using a revised version of the classic sulphuric acid - water nucleation model. All of the nucleated particles are transferred to the smallest aerosol size section. Presentations are made for various temperatures and sulphuric acid and water content.

Primary particulate matter is often a major component of ambient PM10. The model described above is theoretically well suited to simulate concentrations of primary particulate matter in the atmosphere. The inert nature of most primary particles eliminates the need for simulation of chemical transformations and gas-aerosol exchange, which reduces the modelling uncertainties for primary particles. Such simulations were utilised for the simulation of PM10 at the domains of the AutoOil-II domains (DG-ENV, 2001) described below in Figure 3. However, practical constraints on spatial resolution in the regional background and uncertainties in primary PM emissions currently limit the accuracy of primary particle modelling. However, the expected relative gains of the maximum concentrations are represented accurately following the introduction of emission reductions expected between 1995 and 2010.
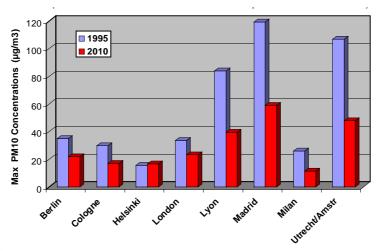

Figure 3. Maximum PM10 concentrations at the AutoOil-II domains in 1995 and 2010

For modelling secondary particular matter the characterization of primary emissions is necessary with detailed information on size and chemical speciation of what exactly is emitted into the air. Such emissions are needed for road dust emissions, vehicle exhaust emissions, construction emissions, wind blown dust emissions, stationary source combustion emissions and even for agricultural PM emissions. Such details are rather difficult to obtain and there are no golden rules of attribution of existing emission data into size bins. At best the size of particle emissions are usually described in four size ranges (<1 μm, 1-2.5 μm, 2.5-10 μm, > 10 μm), which are not sufficiently resolved for modelling purposes.

The lack of size information for particles below 1 μm is especially problematic for combustion sources, where the most emitted particles are expected to be less than 0.2 μm in diameter. For these reasons are urgently needed new measurements for accurately characterizing the size of PM emissions over the full size range. Other reasons for which emission seems to be problematic is the intermittent characteristics of the various source activities, the dependence of emission rates on local environmental conditions (e.g. soil moisture and the extent to which soil surfaces are disturbed), which are not routinely measured and on the strong influence of emissions on wind speed. Emissions models do not generally take such spatial and temporal variations into account.

From parametric studies carried out for sulphur cycle it is clear that 15-20 PM size classes are sufficient for analysing the aerosol spectrum. More classes are needed for small aero-disperse particles. For the purposes of this work and in order to validate the calculations the bins utilised for the size spectrum distribution are shown at the following table.

Table 1. Bins of the Size-Spectrum (μm)

1	2	3	4	5	6	7	8
0.005-0.016	0.016-0.025	0.025-0.039	0.039-0.062	0.062-0.098	0.098-0.156	0.156-0.394	0.394-0.625
9	**10**	**11**	**12**	**13**	**14**	**15**	**16**
0.625-0.992	0.992-1.575	1.575-3.97	3.97-6.30	6.30-10.0	10.0-15.9	15.9-25.2	25.2-40.0

The simulation carried out were initially carried out at the domain of London. These, demonstrated the advantages of solution of the conservation equation for the complete size spectrum and give promising results for improved calculations of secondary PM. New particle formation is influenced by nucleation rate. Unfortunately, the schemes available in literature incorporate differences of several orders of magnitude (Lazaridis et/ al., 1999)). The validity of the classical theory expressions is difficult to confirm either in controlled laboratory studies or through atmospheric measurements for ultra-fine particle dynamics. This remains an essentially unsolved problem which could be dealt only via comparisons of calculated data with measurements (despite the uncertainties of PM emissions at different size distributions).

FINAL REMARKS
The implementation of the aero-disperse conservation equations is possible under the current computational speed. The quality and accuracy of the simulations has been evaluated after implementation of the FIA^2PES^2 module at the CAMx model. This effort concentrated on the sulphuric acid simulations with a new scheme for nucleation. These calculations include diagnostic analysis, appraisal of the utility of the modelling results, and qualitative estimation of uncertainties. Uncertainties in model formulation include specification of the governing gas and aqueous phase chemical mechanisms, and deposition rates of many pollutant species, and estimation of vertical exchange rates and overall mixing depth. Other key sources of uncertainty are the estimates of primary particle emissions, and the boundary conditions.

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