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Quantitative assessment of the effect of surface deposition and coagulation on the dynamics of submicrometer particles indoors.

Shortened running title: Particle deposition and coagulation indoors.

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ABSTRACT

The main focus of this paper is the quantitative assessment of surface deposition and coagulation as mechanisms for reducing particle concentration indoors. Experimental part of the study involved measurements of particle concentration and size distribution using a Scanning Mobility Particle Sizer (SMPS) TSI Inc. Model 3934 in the size range between 0.017 and 0.898 μm. The experiments were conducted in an experimental chamber for three different types of aerosols: environmental tobacco smoke, petrol smoke and ambient air aerosols. Two mathematical models were developed and validated: DECOM and SIMIAQ. The DECOM method was developed to characterise and quantitatively assess the contribution of surface deposition and particle coagulation on particle concentration reduction indoors. A simplified mathematical model (SIMIAQ) was developed for the prediction of particle concentration indoors, which is based on a particle number balance equation using the concept of particle deposition velocity.

A number of conclusions were drawn from this study. The estimates of CMD based on particle coagulation provides relatively accurate results for all aerosols but petrol, with predicted values within 10% of the measured data over a time period of up to two hours. The error in prediction of CMD values for petrol was somewhat larger, up to 30%. The average values for the overall deposition loss rates varied from $4.3\text{x}10^{-5}$ s^{-1} (0.16 h^{-1}), to $1.1\text{x}10^{-4}$ s^{-1} (0.39 h^{-1}). The overall deposition velocities associated with surface deposition and coagulation ranged from $9.6\text{x}10^{-4}$ cm s^{-1}, to $2.4\text{x}10^{-3}$ cm s^{-1} and for the surface deposition only from $2.8\text{x}10^{-4}$ to $6.3\text{x}10^{-4}$ cm s^{-1}. For indoor conditions with an air exchange rate above 1.3 ach, (natural ventilation, no filters) only a reduction in particle number of about 20%, is attributed to the surface deposition and coagulation. It was concluded that the developed models showed very good agreement between measured and predicted values for controlled chamber.

INTRODUCTION

Air filtration and ventilation are the mechanisms considered the most important for reducing particle concentration indoors, however only limited information is available on the assessment of the effects attributed to other mechanisms.

Particle surface deposition which results in reduction of particle number and mass concentrations in the air, and coagulation which reduces particle number, causes particle growth but does not affect mass concentration, are the two mechanisms also considered important for the overall indoor particle dynamics. Mechanisms such as aerosol nucleation, evaporation, condensation are considered to be of lesser significance in terms of affecting indoor processes.

The main focus of this paper is the quantitative assessment of surface deposition and coagulation as mechanisms for reducing particle concentration indoors. The importance of these mechanisms in relation to each other was investigated, as well as in comparison with other removal mechanisms, such as air filtration and ventilation. The quantitative assessment of deposition rates/velocities could be used for modelling purposes, predicting the exposure indoors. The paper objective was to provide answers to the following questions: does the particle coagulation and deposition need to be included in mathematical models predicting the aerosol evolution indoors; and, how to estimate their effect and the input parameters (loss rates) to be used for real–world situations modelling?

To answer the questions stated above, two mathematical models were developed and validated: DECOM and SIMIAQ. The DECOM method was developed to characterise and quantitatively assess the contribution of surface deposition and particle coagulation on particle concentration reduction indoors. Simplified formulas for the prediction of the evolution of particle concentration and size distribution were derived from the analytical expression for surface deposition and coagulation. The DECOM method has been validated with experimental data obtained from chamber studies conducted under different ventilation conditions for different types of aerosols. The thickness of the air boundary layer, a parameter required for the determination of surface deposition, has also been determined from experimental data and compared with data from the literature.

Mathematical modelling is an important tool in predicting exposure and surface contamination by airborne pollutants. A number of models derived mainly from the mass balance of pollutants have been developed. While most of the existing models focus on gaseous pollutants or larger particles (PM_{10}, $PM_{2.5}$ - particulate matter larger than 10 μm and 2.5 μm, respectively), only a few are capable of predicting the evolution of submicrometer particles. There was a need for a model that, on one hand would be capable of providing a sufficiently accurate prediction of an aerosol's characteristics for a broad range of indoor scenarios, and on the other hand, a model relatively simple, applicable and user friendly. A simplified, single zone, mathematical model (SIMIAQ) has been developed for the prediction of particle concentration indoors, which is based on a particle number balance equation using the concept of particle deposition velocity. The model incorporates the effects of ventilation, surface deposition and coagulation, and requires only a limited set of input parameters. The model has been extensively validated with experimental data obtained from chamber studies and real-world measurements.

BACKGROUND

In the absence of indoor emission sources, particle concentration can be estimated from the outdoor particle concentration, air filtration and air exchange rate, the rate of particle removal due to deposition on indoor surfaces, and coagulation rate.

Particle deposition rate λ_d could be characterised using the deposition velocity v_d and the relation: $\lambda_d = v_d.(S/V)$, where S and V are the surface and volume of the enclosure, respectively. The deposition velocity is defined as the flux density of particles towards the surface divided by the concentration of particles in the air away from surface. Knowledge of the deposition velocities, in principle allows for estimation of indoor particle concentration levels from outdoor values and from available building characteristics and operation parameters. There are however, certain limitations in using the concept of deposition velocity for determination of particle deposition. The limitations are related to the assumptions made about uniform concentration of particles in the indoor volume and knowledge of the surface area, which depends on the surface's texture and on the range of surfaces in the indoor environment. This topic is discussed in more details in (Nazaroff et al. 1993).

The direct measurements of deposition rates of submicrometer particles, especially under field conditions, present an experimental challenge, due to the sensitive analytical techniques and long sample collection times required. The obtained data are site-specific and the range of values reported in the literature is broad. Due to the range of, and fluctuations in parameters affecting particle depositions, the deposition velocities of ambient air measured in field conditions exhibit larger scatter and are associated with larger uncertainty than those measured in laboratory/chamber experiments. Chamber studies offer an easier and more rapid method for direct and indirect measurements of deposition rates under controlled conditions, however, caution must be exercised in applying obtained results to real-world environments.

While most of the studies on deposition velocities conducted earlier focused on larger particles (Ligocki et al. 1990), most of the anthropogenic pollution sources are combustion related and generate particles smaller than one micrometer. Submicrometer particles represent the majority of particulate matter dispersed in an urban environment in terms of number concentrations (Morawska et al. 1998; Nazaroff et al. 1990; Ligocki et al. 1990).

Sinclair et al. (1985); Sinclair et al. (1988) and Weschler and Shields (1988) investigated the particle deposition velocities of ionic species inside commercial and residential buildings using bulk chemical analyses. Indirect measurements of size dependent deposition velocities for environmental tobacco smoke (ETS) based on the concentration decay were conducted by Offermann et al. (1985). A review on the deposition of radon decay, equivalent to ultrafine particle deposition was presented by Knutson (1989). Nazaroff and Cass (1989) developed mathematical models for particle deposition on indoor surfaces. Studies on deposition velocities inside laminar flow clean rooms were conducted by Miller et al. (1988); Wu et al. (1989) and others. Due to the specificity of the flow conditions, the results of these studies are not easily transferable to cases of conventional residential, commercial and institutional buildings.

Ligocki et al. (1990) measured deposition rates of submicrometer particles inside five museums using a single particle counting technique (electron microscope equipped with energy and bulk chemical analyses capability). Deposition velocities to vertical and upward-facing horizontal surfaces were determined as a function of particle size from suspended particles onto filters and particles deposited on vertically and horizontally oriented plates. Measured deposition velocities towards vertical surfaces were in the range of 10^{-4} to 10^{-3} cm s^{-1} at all sites, but varied from site to site in terms of their dependence upon particle size.

Deposition velocities towards horizontal surfaces were in the range of 10^{-4} to 10^{-1} cm s^{-1} and showed the expected increase with particle size due to gravitational settling.

Nazaroff et al. (1990) theoretically predicted the deposition velocities for the case of five experimental studies conducted by Ligocki et al. (1990). The deposition velocities were calculated from data on the surface-temperature difference and near-wall air velocity, using idealised representations of the airflow field near the wall. Based on a combination of model predictions and measurement results (as input data), the best estimate of deposition velocity on horizontal surfaces was from 1.3×10^{-3} to 2×10^{-3} cm s^{-1} for particles of 0.05 μm diameter, and from 1×10^{-3} to 3.3×10^{-4} cm s^{-1} for 1 μm particles.

Based on the bulk deposition velocities measured by the anion chromatography technique, Ligocki et al. (1990) reported velocities of sulfate, nitrate and ammonium ions to vertical surfaces of about 10^{-3} cm s^{-1} with time periods of 2 months to a year employed for the collection of particles deposited on walls. Sinclair et al. (1985) found deposition velocities for sulfate onto vertical and horizontal surfaces to be 2.8×10^{-3} and 7.5×10^{-3} cm s^{-1}, respectively.

Van de Vate (1972) measured the deposition velocities for polystyrene particles of different sizes. For submicrometer particles the deposition velocities were in the range between 2.8×10^{-5} to 1.1×10^{-4} cm s^{-1}. The deposition velocities of particles and gases for outdoor conditions were reported by MacMahon and Denison (1979).

Crump and Seinfeld (1981) developed a general theory for the wall loss coefficient in a vessel of arbitrary shape. The particle loss rate is related to particle diffusivity, the particle's settling velocity, the coefficient of the eddy diffusivity and vessel radius. The loss rate does not depend on boundary layer thickness, however the eddy diffusivity coefficient needs to be determined experimentally, unless it can be calculated a priori (Crump et al. 1983).

A mathematical model was developed to simulate the dynamics of indoor aerosols with emphasis on predicting the rate of particle deposition onto surfaces (Nazaroff and Cass 1987; Nazaroff and Cass 1989; Nazaroff et al. 1993). This model is capable of prediction of the time-dependent aerosol size distribution and chemical composition characteristics that depends primarily upon the concentration and composition of outdoor aerosols and on the building ventilation system (Nazaroff et al. 1990). Model calculations for five museum environments showed that generally less than 1% of the fine particles (0.05-2.1 μm) entering the museums were deposited onto the walls.

The deposition velocity of fine particles onto an indoor source depends on the nature of the nearby flow, the intensity of air motion, and the temperature gradient in the boundary layer. Deposition velocity may also vary with other factors, such as surface roughness (Nazaroff et al. 1990). If the airflow regime is known (forced laminar flow, natural convection flow, etc), particle deposition velocities can be related to the mean air velocity along the wall, and the surface-air temperature difference (Nazaroff et al. 1990). When the temperature of a surface is cooler than the temperature of the surrounding air, thermophoresis causes increased deposition of larger particles (Goren 1977). For submicrometer particles the thermophoretic effect is almost size independent (Ligocki et al. 1990).

Indoor air movement results from mechanically induced flows, such as the discharge of air from a ventilation register, or thermally induced flows, such as the flow of air downward along a cold window. Although the nature of indoor airflows has been investigated, the problem is complex and not well understood (Gadgil 1980; Kurabuchi and Kusuda 1987).

Nazaroff et al. (1990), reported overall air velocities at 1 cm from surfaces, in the range from 0 to 30 cm s^{-1}. The surface–air temperature differences were generally in the range of a few tenths to 2 K, and were typically positive in summer (air cooled by HVAC system), and negative in winter (air heated by HVAC systems). For a building with a mechanical ventilation system, the air movement along walls is probably forced by the ventilation airflow. When the system is off, the airflow might be due to natural convection downwards along the cool wall.

The conclusion from the studies conducted by Ligocki, Nazaroff and others, on the deposition velocities as a function of size, is that for particles in the submicrometer size range, the deposition velocity does not depend significantly on size. Thus, considering the range of significant uncertainties associated with the deposition velocity measured under various indoor conditions (temperature, ventilation rate, particles' composition), and the relatively short resident time of particles in real situations (of the order of up to two or three hours), and taking the lack of a significant dependence on size, the particle deposition could be considered constant for all particles in the sumbicrometer size range.

The particle size range in this study was from 0.017 to 0.890 μm. The parameter selected for particle characterisation was count median diameter (CMD). The particle surface deposition was characterised by an average deposition velocity, representing the average value for all particles in the measured size range. The experimental conditions selected for the chamber studies were comparable to the field indoor conditions as presented by Nazaroff et al. (1990). The air movements in the chamber, when the fan was switched off after initial aerosol mixing, were caused mainly by the surface-air temperature difference, which was on average 1.5 K. According to Schlichting (1979), this would induce an air velocity of 17 cm s^{-1}, which is comparable to the mean air velocity 20-25 cm s^{-1} driven by ventilation (Nazaroff et al. 1990).

THEORY OF PARTICLE DYNAMICS

Due to the dynamic particle processes and action of external factors, the characteristics of airborne particles continually change. Understanding of the mechanisms governing particle behaviour is needed to evaluate and predict the effects the mechanisms have on particles' characteristics. The main mechanisms considered in this paper are particle coagulation and surface deposition, (including diffusional deposition, thermophoresis and gravitational settings). The theory of these mechanisms is discussed only briefly as the topic is presented in more detail elsewhere (Hinds 1982; Friedlander 1977; Willeke and Baron 1993). The analytical expressions/formulas, which have been used, are presented in the Appendix.

Coagulation

Coagulation results in an increase in particle size and a decrease in particle number concentration. In the absence of any loss or removal mechanisms, there is no change in mass concentration. The rate of decrease in particle number concentration C for diffusion induced coagulation is expressed in Eq 1A (Appendix).

For monodisperse coagulation the coagulation coefficient K is independent of particle size for larger particles (d_p>1 µm) and increases as particle size decreases for smaller particles. Under common environmental conditions (indoor, ambient air), the extent of the particle size increase is sufficiently limited, K could be considered as a constant, and the rate of coagulation is then proportional to particle concentration squared (C^2). Thus, coagulation is a significant and also a rapid process at high number concentrations and a less significant and slower one at low concentrations. The change in particle size due to coagulation over a period of time *t,* for liquid and solid particles could be approximately calculated using Eq 3A.

Whether or not the coagulation can be neglected, depends also on the time scale under consideration. The time required for number concentration to halve is approximately 0.5, 5.5 and 55 hours for the initial particle number concentrations of 10^6, 10^5 and 10^4 [particle cm^{-3}], respectively (Hinds 1982). The time required for the same concentrations of particles to double their sizes is approximately ten times longer.

Under environmental conditions, the particles are usually polydisperse, and the coagulation process is more complicated than for monodisperse aerosols. The use of Eq's 2A, 3A for polydisperse aerosols requires the use of numerical methods, because the coagulation for every combination of particle sizes has a different value of K and has to be calculated separately. The average coagulation coefficient for polydisperse aerosols with a lognormal size distribution (K_{avg}) can be calculated according to Eq 5A (Zebel 1966; Willeke and Baron 1993). The K_{avg} can be used in place of K in Eq 2A to predict the change in number concentration over a period of time t, for which there is only a modest change in *CMD*. The increase in *CMD* over a time for which K_{avg} is approximately constant can be predicted from Eq 3A. For this type of calculations, it is reasonable to assume that σ_g, the geometric standard deviation remains constant for modest changes in particle size. For larger changes in particle size, calculations can be done as a series of steps with a constant but different K_{avg} for each step (Willeke and Baron 1993).

Kinematic coagulation (relative motion between particles due to external forces rather than by Brownian motion) plays a more important role for particles larger than about 1 μm, and has thus not been considered in this paper (Hinds 1982).

Surface deposition

The interaction of particles with surfaces usually leads to particle deposition, as particles, unlike gas molecules, adhere to the surface once they collide. Thus the main factor affecting particle deposition is their transport to the surface. Particle deposition can be expressed in terms of a deposition velocity v_d, defined as the deposition flux divided by the undisturbed concentration $v_d = J/C_o$. Deposition velocity is the effective velocity with which particles migrate to a surface, and is analogous to the settling velocity for deposition by gravitational settling.

Diffusion is the primary transport mechanism for particles less than 0.1 μm in size and for smaller enclosures. Where the physical scale is large, convection or eddy diffusion of parcels of aerosols greatly exceeds the transport of aerosol particles by diffusion (Hinds 1982).

Deposition onto surfaces by diffusion from turbulent flow is more complicated than when only concentration gradient is present, and cannot be solved explicitly. It is assumed that the turbulent flow provides constant concentration C_o beyond a thin diffusion boundary layer (δ) adjacent to a surface. In the diffusion boundary layer, concentration decreases linearly from C_o to zero at the surface. Under these conditions the deposition velocity is given by Eq 6A. The difficulty in applying the equation lies in the determination of the proper value of δ, which depends on flow mechanics, the nature of the velocity boundary layer, and the size of particles (Davies 1966; Fuchs 1964; Okuyama et al. 1977).

Thermophoresis

Thermophoresis is a process, which causes particles from a warmer gaseous medium to be deposited on colder surfaces. For particles smaller than the mean free path ($d_p<\lambda$), which means for particles smaller than about 0.066 μm, the thermal force is a result of greater momentum transfer from gas molecules on the hot side of the particles compared to the cold side. For small particles ($d_p<\lambda$) the thermophoretic velocity is independent of particle size and directly proportional to the temperature gradient. For larger particles ($d_{p>}\lambda$) the thermophoretic velocity depends on the thermal conductivity of the gas and particles and is a weak function of particle size. The thermophoretic velocity in a unit temperature gradient (1 K cm^{-1}) exceeds the terminal settling velocity for particles smaller than 0.1 μm. Deposition onto surfaces by thermophoresis during a 100 s period in a unit temperature gradient exceeds deposition by diffusion for particles larger than 0.2 μm. The comparison of the effects of thermophoresis, gravitational settling and diffusional deposition on particle concentration are presented in more detail in Hinds (1982).

Determination of surface and coagulation deposition velocities as parameters characterising particle number losses due to coagulation and surface deposition processes.

Based on a particle mass or number balance, the changes in particle concentration in a single room/chamber could be generally described as:

$$\frac{dC_i(t)}{dt} = S_i - L_i \qquad (1)$$

where C_i is the indoor particle concentration [units: particle cm^{-3}; μg cm^{-3}]; S_i and L_i are the particle generation and loss rates, respectively, either for particle number or mass [units: particle s^{-1}; μg s^{-1}]. For a situation where no internal sources are present and no air filtration takes place, Eq 1 could be rewritten as:

$$\frac{dC(t)}{dt} = \lambda_v C_{Out} - \lambda_v C(t) - \lambda C(t) \qquad (2)$$

The two first terms on the right-hand side represent the effect of ventilation, characterised by an air-exchange rate $\lambda_v = Q/V$ [unit: s^{-1}], where Q is the outdoor air flow rate [unit: m^3 s^{-1}], and V is the effective volume of a room [unit: m^3]. The first term is the rate at which outdoors particles, of concentration C_{Out}, are introduced indoors. The second term represents the rate at which indoor particles are exhausted outdoors. The third term reflects the particle losses caused by mechanisms other than ventilation. The rate at which particles are removed (λ) in relation to their number and mass concentrations will be denoted as λ_{Number} and λ_{Mass}, respectively [units: s^{-1}].

If variables other than C are time independent, the solution to Eq 2 is:

$$C(t) = C_{Out} \frac{\lambda_V}{\lambda_V + \lambda}(1 - exp[-(\lambda_V + \lambda)t]) + C(0)exp[-(\lambda_V + \lambda)t] \qquad (3)$$

where $C(0)$ is the initial concentration indoors at time $t = 0$. The first term on the right-hand side of Eq 3 reflects the evolution towards the steady-state concentration $C(\infty) = C_{Out}\lambda_V/(\lambda_V+\lambda)$; the second term reflects the decay of an initial concentration due to removal by ventilation and non-ventilation processes.

The coagulation and particle deposition on indoor surfaces are considered to be the two main mechanisms causing the decay in particle number concentration. The reduction in mass concentration is caused primarily by surface deposition. The effects of other mechanisms such as nucleation, condensation, evaporation and others are not included, as these are considered to be of less significance for the conditions discussed here (particles dispersed in air of room temperature, and at under-saturated conditions).

Based on the assumptions made above, the particle loss rates λ_{Number} and λ_{Mass} from Eq 2 could be expressed as:

$$\lambda_{Number} = \lambda_{SD} + \lambda_{CG} \qquad (4)$$

$$\lambda_{Mass} = \lambda_{SD} \tag{5}$$

where λ_{SD} *and* λ_{CG} are the loss attributed to the surface deposition (SD) and coagulation (CG) rates, respectively.

The contribution of these mechanisms to the overall particle loss rate λ_{SD} could be expressed as

$$\lambda_{SD} = \lambda_{Grav} + \lambda_{Diff} + \lambda_{Therm} = \frac{v_{Grav}}{H} + \frac{S}{V}\left(v_{Diff} + v_{Therm}\right) \tag{6}$$

where λ_{Grav}, λ_{Diff}, λ_{Therm} (unit: s^{-1}) and v_{Grav}, v_{Diff} and v_{Therm} (unit: cm s^{-1}) are the particle loss rates and deposition velocities induced by gravitation, diffusion, and thermophoresis, respectively; S (unit: m^2) is the indoor surface area; and H (unit: cm) is height of the enclosure.

The particle loss rate due to diffusion and thermophoresis is expressed using the concept of deposition velocity as presented by Hinds (1982) and Nazaroff et al. (1993). It is assumed that particle concentration throughout the room is uniform (perfect mixing of aerosols), except for a thin diffusion boundary layer lining the solid surfaces.

The deposition velocities could be assessed directly by measuring the deposition flux density and particle concentration in the air or indirectly, by monitoring particle concentration evolution under defined conditions (Nazaroff et al. 1993). The thickness of the diffusion boundary layer, δ could be in the first instance estimated from Eq 6A. Using the experimentally determined average deposition rate λ_{SD}, and known values of other parameters included in Eq 7A (Willeke and Baron 1993), δ can be calculated with better accuracy.

The overall surface deposition velocity ($v_{SD} = v_{Grav} + v_{Diff} + v_{Therm}$), presented in this paper, was based on monitoring of particle concentration decay as a function of time for an initially elevated concentrations indoors. Assuming that the initial concentration is much higher than the steady state concentration ($C(0) >> C(\infty)$), the first term on the right–hand side of Eq 3 could be neglected. The deposition velocity could then be calculated from the slope ($b1$) of a linear least-squares regression line fitted to $ln(C(t)/C(0))$ vs time as: $v_{SD} = -(b1+\lambda_v).(S/V)$. The ventilation rate λ_v may be determined in a similar experiment using a non-reactive tracer gas ($v_{SD} = 0$), or by other techniques. In this study λ_v was calculated from the known airflow and room volume.

EXPERIMENTAL

Instrumentation and methodology

Particle concentration and size distribution were measured using a Scanning Mobility Particle Sizer (SMPS) TSI Inc. Model 3934. The system consists of an electrostatic classifier and a condensation particle counter (CPC). Particles are classified according to their electrical mobility, allowing only particles of a selected mobility to pass to the CPC where they are counted after being sufficiently enlarged by vapour condensation. For these measurements the instrument was set up to measure particles in the size range between 0.017 and 0.898 μm.

The experiments were conducted in an experimental chamber of cubicle shape ($V = 3$ m^3), the inner walls of which were covered with several layers of latex paint; the texture of the surface was relatively smooth. Tested aerosols were introduced into the middle of the chamber by a set of manifolds, and then mixed by a fan located inside. To achieve uniform initial distribution of the tested aerosol, a mixing fan was operated during, and 5 minutes after the end of the aerosol generation process. The air and wall temperatures were monitored by two thermistors. One thermistor was mounted on the wall with a thermal joint; the second was exposed to the air at approximately 5 cm from the wall. The sampling point for the SMPS was close to the middle of the chamber.

The experiments for all types of aerosols were conducted under close to zero (closed chamber) ventilation conditions and for environmental tobacco smoke (ETS) also under 0.5 h^{-1} ventilation rate. The laboratory air delivered into the chamber was filtered by a HEPA filter.

Three different types of aerosols were used in this study as the tested aerosols: environmental tobacco smoke, petrol smoke and ambient air aerosols. Environmental tobacco smoke was generated by a smoke generator (Morawska et al. 1997). The system allows generation of sidestream (SS) and mainstream (MS) tobacco smoke, simulating different smoking patterns. In this study a mode of 2 puffs min^{-1}, each of 2 sec duration, was selected. One cigarette was smoked during each run, and both the SS and MS were introduced into the chamber. Petrol smoke was generated using a portable unleaded petrol engine power generator (Honda M3000). The generator operated for 10 minutes to warm up, and was then connected to the chamber for approximately 10 s. The air from a naturally ventilated laboratory where the experimental chamber was located, was used as the source of ambient air tested aerosol. The chamber was first purged with filtered air, and then with laboratory air.

Each monitoring run was conducted according to the following procedure: (i) the chamber was purged with cleaned air; (ii) tested aerosol was introduced into the chamber and mixed for 5-10 minutes; (iii) particle concentration, size distribution, and temperature parameters were then monitored for up to 5 h which is more than the residence time of air indoors for most environments. The sampling frequency was 5 minutes.

RESULTS AND DISCUSSION

Evolution of particle characteristics measured in the experimental chamber

Particle loss rates and deposition velocities were determined from the evolution of particle number and volume characteristics monitored under controlled conditions in the experimental chamber. The size distributions of ETS and of petrol smoke were unimodal and lognormal, and ambient air aerosols, had poly-disperse characteristics. Table 1 presents the initial characteristics of the tested aerosols (*C(0), CMD(0)*).

Figures 1 presents the evolution of total number concentration *C(t)* for individual runs where the curve is normalised by the initial value of *C(0)*. As expected from theory, particle concentration decreases exponentially with time. Trendlines fitted to data over a 5 hour period, show a high correlation, with R^2 within the range from 0.90 to 0.99. The evolution of ambient air concentration shows the largest fluctuations (R^2 = 0.90), resulting from the low initial concentration, thus relatively increasing the effect of random data variation.

It can be seen from inspection of Figure 1 that despite a high level of correlation between measured data and the trendlines, the actual loss rate varied over the time (5 hours). The decay rate in the particle concentration for the first 0.5-1.0 hour was more rapid than shown by the trendlines, and started to lag behind after approximately 4 hours. This could be associated with changes in the coagulation rate, which varies with concentration, as $dC/dt \sim -C^2$ (K~constant; Eq 1A). Higher initial concentration results in higher coagulation rate, a parameter decreasing with time, as concentration decreases. The time changes in surface deposition rate were not significant. The overall loss rate for individual runs could be affected not only by the initial concentration, but also by other particle characteristics such as the size characteristics (CMD), the age of the aerosols, their reactivity, temperature, humidity, presence of other constituents (such as low-pressure volatile gases) and others. The highest values of λ_{Number} for petrol smoke, even though it did not have the highest initial concentration could be associated with these factors.

Figure 2 shows the overall particle deposition rates λ_{Number} assessed for different time intervals. The presented values $\lambda_{Number}(t_i)$, correspond to the middle of the time intervals, over which the deposition rates were estimated (from a trendline fitted to data within that interval). For example, the loss rate associated with a time of one hour was obtained from the exponential equation fitted to measured data over the period of two hours.

The particle changes in the size distribution could be characterised by the changes in the CMD as presented in Figure 3. CMD(t) values are normalised by the initial values of CMD (0). In all cases the CMD shifted towards larger values which can be associated mainly with particle coagulation mechanism. The initial CMD for ETS increased by up to 10%, and up to 40 %, over the intervals of one and five hours, respectively. The changes in ambient air aerosol were less significant (less than 5% and 20%), as the particle concentration was low and particles were already aged. In the case of petrol smoke, the CMD increased to 135%, and up to 210% of the initial CMD, after the same time intervals. The faster growth observed for petrol smoke could be associated with differences in initial characteristics compared with other aerosols: relatively smaller CMD, higher concentrations, younger age and larger reactivity. The method of generation could also affect the growth velocity (presence in the chamber of other combustion products, such as low vapour pressure gases). Changes in CMDs due to coagulation mechanisms were calculated from Eq 3A. Assuming polydisperse coagulation, the CMD values were calculated in time steps, with K_{avg} determined from data measured in a corresponding interval. The ratio between the calculated and measured CMDs for each run are presented in Figure 4. For ETS (ventilation rate VR~0 ach), and ambient air, the calculated CMD values were slightly lower than measured. Calculated values differed from measured by less than 10%, and 15% over 2, and 5-hour monitoring intervals, respectively. An opposite trend was observed for the CMD of ETS measured under ventilation mode (VR~0.5 ach) where particle coagulation slowed down, resulting in an approximately 5% over-prediction of CMD over 2 hours compared with measured data. Calculated values of CMD for petrol smoke were approximately 70% and 55% of the measured values after 2 and 5 hours respectively, indicating that the effect of other mechanisms contributing to particle growth was significant in this run. The observed trends could be attributed to chemical and physical interactions between particles and low vapour pressure volatile gases introduced into the chamber during aerosol generation.

It could be concluded that the estimates of CMD based on particle coagulation provide relatively accurate results for all aerosols but petrol, with predicted values within ± 10% of the measured data over a time period of up to two hours. The error in prediction of CMD values for petrol was somewhat larger, up to 30%.

Qualitative and quantitative assessment of surface deposition and coagulation loss rates/velocities

Figures 5 present the dependence of deposition rates $\lambda_{Number}(t_i)$ on particle concentration for individual runs. The measured λ_{Number} decreased with a decrease in particle concentration, reflecting the effect of coagulation and surface deposition. The loss in particle number concentration was attributed mainly to two mechanisms – particle surface deposition (SD) and particle coagulation (CG). A simple method (DECOM) has been developed to determine the contribution of each of these two mechanisms. Their contribution to the observed overall loss rate was estimated from the evolution of particle volume and number characteristics, measured simultaneously. While the SD reduces both the number and volume concentrations, the CG reduces only the particle number. Thus the difference between these two loss rates provides the coagulation loss rate (Eq 4;5). Using this concept, the deposition rates and velocities attributed to surface deposition and coagulation mechanisms were calculated for the various time intervals for each run.

Figure 6 presents the evolution of SD and CG deposition rates assessed for petrol smoke (VR=0) at four different time intervals. The deposition velocity due to coagulation decreased with time (following a decrease in coagulation rate due to particle concentration decay), and the surface deposition velocity slightly decreased. Similar behaviour was also observed for measurements with other aerosols.

The average values of particle loss rate, deposition velocities and the fraction attributed to each of the mechanisms are presented in Table 1 and Figure 7. The average values for the overall loss rates (SD + CG) varied from $4.3\mathrm{x}10^{-5}$ s^{-1} (0.16 h^{-1}), to $1.1\mathrm{x}10^{-4}$ s^{-1} (0.39 h^{-1}). The overall deposition velocities associated with surface deposition and coagulation ranged from $9.6\mathrm{x}10^{-4}$ cm s^{-1} to $2.4\mathrm{x}10^{-3}$ cm s^{-1} and for the surface deposition only from $2.8\mathrm{x}10^{-4}$ to $6.3\mathrm{x}10^{-4}$ cm s^{-1}. The relatively large variation for each experimental run (20% to 50%) was caused by the time dependency of these parameters (as discussed previously). As can be seen from Figure 7, the measured deposition velocities differ by no more than about a factor of 2.5. This is a small difference compared to the orders of magnitude of difference presented in the literature. This may indicate that neither particles' origin or variation in initial parameters significantly affected the variation in deposition rates for submicrometer particles.

The relative contribution of surface deposition and coagulation on particle number loss could be estimated using the deposition velocities associated with these mechanisms (v_{SD}, v_{CG}). The values of v_{SD}, v_{CG} were normalised by the overall deposition velocity v_{SD+CG} (Table 1). The results from all runs except ambient air, indicate that coagulation dominated the surface deposition mechanisms, with approximately 64-84% of the overall particle number reduction being caused by coagulation. For ambient air, the effect of coagulation was much smaller, of about 34%, which could be associated with very low initial particle concentrations (< 2.7×10^3 particle cm^{-3}) and a larger variation (about 25%) in the deposition velocity values. The average outdoor concentration levels in the urban environment are usually 3 to 5 times higher (Morawska et al. 1998) than the ambient air concentration measured in the chamber.

Figure 8 shows a comparison between deposition velocities measured in this study and reported in the literature. It can be seen that the results are comparable and within the range of the deposition velocities reported by Ligocki et al. (1990) and Nazaroff et al. (1993). Wallace (1996) reported loss rates of 8.33×10^{-5} to 1.39×10^{-4} s^{-1} (0.3 to 0.5 h^{-1}) measured in a real indoor environment. These values are in good agreement with the values of 0.16 $h^{-1}$to 0.39 h^{-1} calculated here. Based on results from a large PTEAM study, the deposition loss rate for sulfur $PM_{2.5}$ was around 4.44×10^{-5} s^{-1} (0.16 h^{-1}) (Wallace 1996). The deposition velocities for sulfate particles reported by Sinclair et al. (1985) are 5-30 times larger. This could be due to the use of a different measuring technique (ion chromatographic method), the use of metallic surfaces as the deposition substrates, or to the lack of data on ambient concentration of the species for most of the deposition periods. Results presented by Van de Vate (1977) for polystyrene particles are approximately 3-20 times smaller than the presented here values. This could be due to differences in measuring technique and experimental conditions where artificially generated polystyrene spheres were introduced into a small steering vessel (1 m^3) and the loss rate was estimated from the decay in particle concentration, determined from electron micrographs of the loaded grids.

Good agreement between the presented results, and the results obtained experimentally by Ligocki et al. (1990) and theoretically by Nazaroff et al. (1990) confirms the validity of the presented method for the determination of the deposition velocity. The deposition rates obtained using this method can be applied for: determination of the particle number and mass concentration for the purpose of exposure assessment, assessment of the effect of surface deposition and particle coagulation on particle dynamics, and quantitative characterisation of these processes through the deposition velocity parameter. The information is available within a relatively short sampling time, is comprehensive and of sufficient accuracy compared to other available methods.

Comparison between the reduction in particle number concentration by ventilation, surface deposition and coagulation mechanisms.

The reduction in particle number due to surface deposition and/or coagulation could be compared with the particle losses due to ventilation. Expressing the particle losses associated with surface deposition, coagulation and ventilation, using the deposition velocity/rate as discussed above, the relative contribution of these mechanisms to the reduction in particle number can be estimated.

The ventilation rate depends on building type, design, construction, operational parameters, ambient conditions such as terrain or wind conditions and on indoor activities (Wallace 1996). In naturally ventilated buildings, such as in residential dwellings, the ventilation rate (Q/V) could vary from 0.1 ach ($2.8\mathrm{x}10^{-5}$ s^{-1}) for extremely tight buildings, up to 40 ach ($1.1\mathrm{x}10^{-2}$ s^{-1}) for very leaky buildings. The average ventilation rate in naturally ventilated houses measured in the PTEAM study (Clayton et al. 1993) varied from 0.3 to 2.2 ach, depending on the geographic location, season, and time of day (day vs night). Murray and Buyrmaster in Wallace (1996) calculated an arithmetic and geometric mean of air exchange rates assessed from 2844 houses throughout the US of 0.76 and 0.53 ach with a geometric standard deviation of 2.3. In warmer regions, such as South Bay of Los Angeles, the air exchange rates could be higher, with average values around 2.2 ach (Wallace 1996). Even larger ventilation rates with an average values larger than 5 ach, have been reported in a study conducted in subtropical city of Brisbane, Australia, which included measurements of ventilation rates in 14 residential houses (Hitchins 1999). Air-conditioned homes typically have lower air exchange rates than naturally ventilated buildings. In the PTEAM study based on the measurements in 147 houses, the average ventilation rate was approximately 0.8 ach (Wallace 1996). The ventilation rate typical for large mechanically ventilated buildings (offices), is approximately 1 ach. In a case study by Jamriska and Morawska (1996) the ventilation rate of a typical mechanically ventilated office building in Brisbane was 0.8 ach.

The ventilation rate can be considered also as a loss rate parameter (Eq 2). It could be compared with particle loss rate due to surface deposition and coagulation. Table 2 shows ventilation rates and ratios of deposition velocities to the ventilation rates for a range of air exchange conditions as discussed above. The deposition velocities were calculated as $v_d = \lambda_d * V/S$, assuming the ratio S/V~3 m^{-1} (Wallace 1996). The ratios corresponding to different removal mechanisms, express the relevant contribution/significance of these mechanisms to the overall reduction in particle number. It can be seen that ventilation is the most dominant particle removal mechanism for all cases when VR > 0.8 ach. Only for minimum ventilation (VR = 0.1 ach), do the effects of CD and SD prevail. For ventilation rate of 5 ach, particle losses due to ventilation are up to 74, 23 and 20 times higher than due to SD, CG and the combined effect of both, respectively. Coagulation dominates over surface deposition, and shows an approximately 3 times larger contribution to particle losses when compared with SD. For example, at the VR = 0.5 ach, the v_{CG} represents 44% of the v_{vent}, compared with 14% associated with the v_{SD}. The combined effect of CG and SD at the same VR is approximately 52%. Setting a value of 20% as the level where the effect of a mechanism could be considered as significant, the effect of SD, CG and the combined effect of both could be neglected for air exchange rates of 0.4 ach, 1.1 ach and 1.3 ach, respectively (Figure 9).

Data presented in Tables 1 and 2 could be used for qualitative (in relation to the question: “should the mechanisms be considered? ”), and quantitative (“what is the particle loss rate? ”) assessment of particle losses due to ventilation, coagulation and surface deposition. The values of deposition velocities could be used as input parameters in indoor air quality mathematical models.

In cases where supply air contains recirculated and filtered air, the relative contributions of SD and CG to the overall reduction in concentration is decreased even further.

It can be concluded that the significance of CG and SD needs to be assessed together with the effect of ventilation and air filtration mechanisms. For naturally ventilated indoor environments and with an air exchange rate above 1.3 ach, only a reduction in particle number of about 20%, is attributed to SD and CG. In terms of particle mass reduction, which results from surface deposition and ventilation but not coagulation, the ventilation dominates over the SD, which for VR≤ 0.3 ach, represents less than 23%. While the effect of SD and CG needs to be taken into account for indoor surface contamination, the concentration levels and thus exposure are dominated by ventilation and filtration mechanisms.

Particle reduction due to coagulation: measured results vs theoretical prediction

The relationship between measured and predicted evolution of total number concentration has been investigated and the contribution of individual mechanisms (SD, CG) in overall reduction of particle number concentration assessed. The general findings are demonstrated on the example of the results for the ETS (VR = 0 ach), measurements. A comparison between measured and predicted evolution of *C(t)* over 5 hours is presented in Figure 10. A similar pattern was observed for measurements with other aerosols. The theoretical prediction of *C(t)* is based on Eq 3, where the average values of particle loss rate for each mechanism (Table 1) were used as the removal rate λ in the equation. When predicting *C(t)* for one mechanism, the removal rates for the remaining mechanisms were assumed zero. It can be seen from Figure 10 that the predicted effect of SD on *C(t)* is smaller than the effect of CG. For example, the concentration predicted for $t = 1$ hour, assuming only the effect of SD, was about 5% lower that the measured initial concentration C(0), and 14% lower for only CG. The measured concentration decreased by 20% of its initial value in the same period of time. The predicted C_{SD+CG} concentrations are slightly larger, (less than 5%), than the measured values during the first 3 hours of the measurements, and slightly smaller than the measured during the rest of the measuring interval. As discussed previously, this is due to the changes of the deposition rate related to changes in the characteristics of the particle system with time, the effect not taken into account, as only average values were used for the prediction.

While the predicted evolution of particle number concentration in Figure 10 was based on the experimentally determined parameters (loss rates λ_{SD}, λ_{CG}, λ_{Number}), Figure 11 presents the evolution based on theoretically predicted values. Particle concentration was predicted from Eq 2A with the coagulation coefficient *K* (monodisperse aerosols) and K_{avg} (polydisperse aerosols) determined from Eq 4A and Eq 5A, respectively. Depending on the assumed conditions of aerosol size distribution and time dependency of CMD, the particle concentration C_{CG} was predicted for several cases. C_{CG} denotes particle concentration affected by coagulation mechanism only (the effect of surface deposition is not included). The following cases were investigated and annotation used: C_{CG} *(case*A) - monodispese aerosols, constant CMD~*CMD(0)*; C_{CG} *(case B*) – monodisperse aerosols, *CMD(t)*; C_{CG} *(case*

C) – polydisperse aerosols, $CMD(t)$, $\sigma_g(t)$. The C_{CG} prediction based on the experimentally determined particle coagulation loss rates (λ_{CG}) is denoted as C_{CG} *(case Exp)*.

For the time independent caseA, the changes in the input parameters were neglected, and the initial $C(0)$, $CMD(0)$ and $\sigma_g(0)$ were used as the input values. For the time dependent scenario ($CMD(t)$ and $\sigma_g(t)$ - functions of time) the evolution of $C_{CG}(t)$ was calculated in time steps for different intervals. Particle concentration at time t_i, $C_{CG}(t_i)$ was calculated from the calculated concentration $C_{CG}(t_{i-1})$ and the measured values of $CMD(t_i)$ and $\sigma_g(t_i)$. For i=1(1st time interval) the initial values of $C(0)$, $CMD(0)$ and $\sigma_g(0)$ were used as the input parameters.

It can be seen from Figure 11 that all data series C_{CG} are similar, with the difference in concentrations smaller than 10% over the 5 hour monitoring interval. C_{CG} *(case C)* shows the closest fit to the measured $C(t)$ values, however the differences in comparison with the predictions for the other cases, are not significant. The C_{CG} *(case A)* follows very closely the C_{CG} *(case Exp)* evolution. The C_{CG} *(case B)* slightly over-predicts C_{CG} *(case Exp),* and the values of C_{CG} *(case C)* are slightly underpredicted in comparison with C_{CG} *(case Exp).* It can be concluded that the evolution of C_{CG} could be estimated by any of the presented methods (case A, B, C, Exp).

Considering the prediction accuracy and the calculation simplicity, the C_{CG} could be predicted using the assumptions of particle monodispersity and constant CMD (case A). This method offers the simplest and relatively accurate assessment of C_{CG}.

Determination of the thickness of the air boundary layer

The knowledge of the thickness of the particle diffusion concentration boundary layer σ is required for establishing if the losses due to particle diffusion onto a surface are negligible for an aerosol of a certain size. The smaller the value of σ the larger is the influence of diffusion deposition.

The range of σ reported in literature is very broad. Several studies reviewed by Van De Vate (1972) report σ values between 1 μm to 2.3 mm. The same author also measured the thickness of the diffusion boundary layer in a containment with natural convection. Assuming that aerosols are deposited by diffusion and gravity, the determined σ for polystyrene spheres of a diameter in the range from 0.09 to 1.30 μm was 850 μm. This result was in good agreement with the theory of stirred diffusion. Nazaroff and Cass (1987) experimentally established the thickness of the boundary layer to be in the range from 20 to 600 μm for particle diameters in the range from 0.1 to 1.0 μm and temperature difference in the range –1 to 1 K.

The thickness of the boundary layer σ in this study was estimated from Eq 6 and 7A. The gravitational settling velocity v_{Grav} and the thermophoretic velocity v_{Therm}, were calculated according to Hinds (1982) and Willeke(1993) using *CMD(t=0)* as an input parameter and then conducting calculations for this particular size. The average value of the measured surface deposition rate (Table 1) was used as the λ_{SD} parameter. The temperature difference between the walls and the air inside of the chamber was -1K (T_{wall}~292 K).

The calculated σ values were: 861 μm for ETS (VR = 0 ach), 45 μm for ETS (VR = 0.5 ach), 626 μm for petrol smoke and 897 μm for ambient air aerosols. The lowest value could be associated with airflow within the chamber causing a reduction of σ. Excluding the measurement for ETS (VR = 0.5 ach) narrows the range of the boundary layer thickness from about 630 to 900 μm. These results are comparable with the Van De Vates' (1972) results and in good agreement with results reported by Nazaroff and Cass (1987). This indicates that the developed simple method of assessing the thickness of the boundary layer is applicable for the estimation of σ with reasonable accuracy. The measured values of σ could be used as a good estimate of the parameter in mathematical models in cases where indoor conditions are similar to those presented here. Where conditions are significantly different, the presented method provides tools for indirect assessment of the parameter.

The contribution of gravitational settling, diffusion and thermophoresis on particle surface deposition .

The relative contribution of gravitational settling, diffusion and thermophoresis could be assessed by comparing the values of deposition velocities (v_{Grav}, v_{Diff}, v_{Therm}) associated with these mechanisms, with the measured SD velocity (v_{SD}). The summary of the deposition velocities is presented in Table 3. The gravitational force has the smallest effect on particle deposition, as expected for submicrometer particles of CMD in the range from 0.035 to 0.111 μm. The deposition velocity associated with gravitational force was less than 6 % when compared with the overall measured SD velocity.

The diffusion related deposition velocity varied from 25% to 83%, and for thermophoresis, the range was from 25% to 77%. Thus the effect of both these mechanisms (diffusion and thermophoresis) is comparable, and needs to be considered for the calculation of particle concentration reduction and σ values. For conditions where a larger temperature gradient is present, such as for example in an air-conditioned indoor environment, the effect of thermophoresis would be more significant.

Simple model for prediction of particle concentration indoors (SIMIAQ) and prediction of the overall deposition loss rates.

Based on the theory presented above, the concentration of particles indoors at a certain time *t* can be calculated. The input parameters required by the model in relation to particles are *C(0)* and *CMD(0)* and in relation to the indoor environment, surface to volume ratio, the temperature of the walls and of indoor air. For most indoor environments S/V~3 m^{-1}, and ΔT~1K (Wallace 1996; Nazaroff et al. 1993). The values of σ presented in Table 3 can be used for the calculations, or this parameter can be measured on site using the presented method.

In real environments where air infiltrating from outside contains particles and indoor sources are present, the situation is more complex. For this scenario an extended version of SIMIAQ model could be applied (Jamriska et al. 1999). In addition to the discussed loss mechanisms, the model also incorporates particle generation mechanisms, such as the introduction of particles from outdoors (supply air, infiltration) and from indoor sources, and the effect of air filtration on particle concentration. The model has been tested for real-world conditions in a large air-conditioned indoor space of an office and hospital building and showed good agreement between measured and predicted values (Jamriska et al. 1998).

For indoor conditions with no filtration, the evolution of particle concentration could be calculated according to Eq 3. Determination of particle losses and surface deposition due to different mechanisms could also be calculated from Eq 3, using the loss rates associated with gravitational settling, diffusion, and thermophoretic depositions.

The SIMIAQ model was tested in chamber studies and for a naturally ventilated indoor environment. The monitored evolution of characteristics of particles generated by cooking (frying eggs, and capsicum) in the kitchen of a residential house, was compared to the model predicted evolution. The testing was conducted under usual for this house indoor conditions with semi-opened windows. The ventilation rate was assessed by applying a tracer gas-SF6 decay technique in parallel with the measurements of particle characteristics, and was 1.55 h^{-1}. Initial particle concentration was 2.02×10^5 [particle cm^{-3}], initial *CMD(0)* was 0.047 μm. Outdoor air concentration $C_{Out}(0)$ and $CMD_{Out}(0)$ were 1.31×10^4 [particle cm^{-3}] and 0.055 μm, respectively. The other input parameters used in the calculations were: S/V~3 m^{-1}, ΔT~1K, T_{air}~293 K, particle density ~1 g cm^{-3}, and σ~ 800 μm.

The calculated particle loss rates associated with gravitational settling, diffusion, thermophoretic and coagulation losses (Eq 6, 7A) were: λ_{Grav} ~1.1×10^{-7} [s^{-1}], λ_{Diff} ~4.6×10^{-6} [s^{-1}], λ_{Therm} ~8.0×10^{-6} [s^{-1}], λ_{CG} ~2.91×10^{-4} [s^{-1}]. The overall loss rate, λ_{Number} of 3.0×10^{-4} [s^{-1}] was dominated by coagulation and was comparable to but lower than the ventilation rate λ_{vent}, of 4.3×10^{-4} [s^{-1}]. In this case the most significant particle reduction mechanisms were ventilation and particle coagulation. The prediction was conducted only for a short period of time (15 minutes), as only limited experimental data were available. Particle evolution was predicted by the SIMIAQ model using the simple monodisperse coagulation mode (Eq 2A; 3; 3A) and the minimum input parameter method (CMD(0) used as size parameter for all particles in the investigated size range). The values of particle concentration and CMD at the end of this interval were: C_{meas}~1.0×10^5 [particle cm^{-3}], C_{Pred}~1.2×10^5 [particle cm^{-3}], CMD_{meas}~0.055 μm; and CMD_{Pred}~0.050 μm. The predicted concentration was approximately 18% higher than measured. This could be associated with changes and uncertainties in the input parameters (ventilation rate, uniform distribution of air flow indoors), and the method's limitations (assumption about a simple monodisperse coagulation mode, under-prediction of particle deposition due to air turbulence). In terms of size characterisation, the model under-predicted the CMD values by approximately 10%.

It could be concluded that the model showed very good agreement between measured and predicted values for controlled chamber conditions and relatively good agreement for field conditions. It offers a simple and relatively accurate tool for predicting particle evolution indoors. It could be applied for indoor exposure assessment and for the estimation of the surface deposition of airborne material. While the focus of paper was on submicrometer particles, it could be extended for particles of a broader size range.

CONCLUSIONS

The main focus of this paper was the quantitative assessment of surface deposition and coagulation as mechanisms resulting in reduction of particle concentrations indoors. The importance of these mechanisms in relation to each other was investigated, as well as in comparison with other removal mechanisms. The quantitative assessment of deposition rate/velocities could be used for modelling purposes and predicting the indoor exposure.

Evolution of particle characteristics of environmental tobacco smoke, petrol smoke and ambient air aerosols was investigated in an experimental chamber under controlled conditions. Based on continuous monitoring of particle number and calculated mass concentrations an indirect method for assessment of particle loss rate due to surface deposition and coagulation has been developed. Deposition velocities of the tested aerosols determined by the method, were in good agreement with the results reported from direct real-world measurements indoors, and also with theoretical predictions. The developed method offers a simple and relatively accurate tool for characterisation of particle evolution. In summary, for indoor conditions with ventilation rates higher than 1.3 ach, the ventilation effect prevails over particle loss due to coagulation and surface deposition, with approximately 80% of particle losses attributed to ventilation. Coagulation losses depend on particle concentration and residence time, and dominate over particle surface deposition. The effect of air filtration needs to be considered separately and is beyond the scope of this paper.

A simple mathematical model for prediction of the evolution of particle concentration and CMD was developed and validated. The latter was used as a single parameter characterising the overall changes in particle size distribution. The model, based on a particle number balance equation, combines the deposition velocity concept with basic formulas describing particle dynamics. The model has been tested using chamber and field data and showed relatively good agreement between measured and predicted data.

A formula describing the contribution of gravitational settling, diffusion and thermophoresis to the overall surface deposition has been derived. It allows theoretical calculation of the particle accumulation on surface of materials. Applying experimental chamber data to the formula, the thickness of the air boundary layer has been determined. While this parameter depends on surface roughness, and may vary significantly under different field conditions, chamber data were in reasonable agreement with published data. This method is easily applicable in field conditions.

Although the application of measured results to real-world situations needs to be performed carefully as the indoor conditions may differ significantly to the ones presented, the paper provides an approximate range of input parameters for mathematical modelling, and more importantly, it presents an insight and means for evaluating the effects of mechanisms governing particle behaviour indoors.

NOMENCLATURE:

C - particle number concentration [particle cm$^{-3]}$

C_o - initial particle concentration [particle cm$^{-3]}$

C_c - slip correction factor [-]

CMD - count median diameter [μm]

D - particle diffusion coefficient [cm^2 s^{-1}]

d_p - particle diameter [μm]

d_o - initial particle diameter ($t=0$) [μm]

g - gravitational acceleration [cm s^{-2}]

H - height of a room [cm]

J - particle deposition flux [particle cm^{-2} s^{-1}]

k - Boltzman constant $1.38\text{x}10^{-23}$ [N m K^{-1}]

K - coagulation coefficient for monodisperse coagulation [cm^3 s^{-1}]

K_{avg} - coagulation coefficient for monodisperse coagulation [cm^3 s^{-1}]

S - surface area of the enclosure [m^2]

T - absolute temperature of gas [K]

∇T - temperature gradient [K cm^{-1}]

V - volume of the enclosure [m^3]

Greek letters.

δ - thickness of air boundary layer [cm]

λ - gas mean free path [μm]

λ_{Number} - particle number loss rate [s^{-1}]

λ_{Mass} - particle mass loss rate [s^{-1}]

λ_d - particle deposition rate [s^{-1}]

λ_v - ventilation rate [s^{-1}]

λ_{Diff}, λ_{Grav}, λ_{Therm} - particle loss rate due to diffusion, gravitation and thermophoresis [s^{-1}]

v_d - particle deposition velocity [cm s^{-1}]

v_{Diff}, v_{Grav}, v_{Therm} - diffusional, thermophoretic and gravitational settling velocity [cm s^{-1}]

σ_g - geometric standard deviation of particle size distribution

η - gas viscosity [g cm^{-1} s^{-1}]

ρ_p - particle density [g cm^{-3}]

ρ_g - gas density [g cm^{-3}]

Abbreviation.

CG - coagulation

SD – surface deposition

APPENDIX

The change in particle number concentration due to coagulation resulting from Brownian motion

$$\frac{dC}{dt} = -KC^2 \tag{1A}$$

A general solution to Eq 1A

$$C(t) = \frac{C_o}{1 + C_o Kt} \tag{2A}$$

The change in particle size due to coagulation for liquid and solid particles

$$d(t) = d_o(1 + C_o Kt)^{1/3} \tag{3A}$$

Coagulation coefficient K for monodisperse aerosols (Hinds 1982):

$$K = 4\pi d_p D = \frac{4kTC_c}{3\eta} \tag{4A}$$

Coagulation coefficient K_{avg} for polydisperse aerosols of lognormal size distribution (Willeke and Baron 1993):

$$K_{avg} = \frac{2kT}{3\eta}\left[1 + e^{\ln^2\sigma_g} + \left(\frac{2.49\lambda}{CMD}\right)\left(e^{0.5\ln^2\sigma_g} + e^{2.5\ln^2\sigma_g}\right)\right] \tag{5A}$$

The particle deposition velocity is expressed as (Hinds 1982)

$$v_d = \frac{D}{\delta} \tag{6A}$$

The overall particle deposition rate (see Eq 6) due to gravitational settling, diffusion and thermophoresis (Hinds 1982; Friedlander 1977; Willeke and Baron 1993; Van de Vate 1972) could be expressed as :

$$\lambda_{SD} = \left\{\frac{\rho g}{18\eta h} d_p^2 + \frac{SkT}{3\pi V\eta}\frac{1}{\delta}\frac{1}{d_p}\right\} C_c\left(d_p\right) + \frac{S}{V}\frac{k_1.k_2.k_3.\eta.\nabla T}{\rho_g.T} \tag{7A}$$

for $d_p < \lambda$: $k_1 = 0.55$; $k_2 =$ k3 = 1

for $d_p > \lambda$: $k_1 = 1.50$, $k_2 = C_c$, k_3 = molecular accommodation coefficient

FIGURES

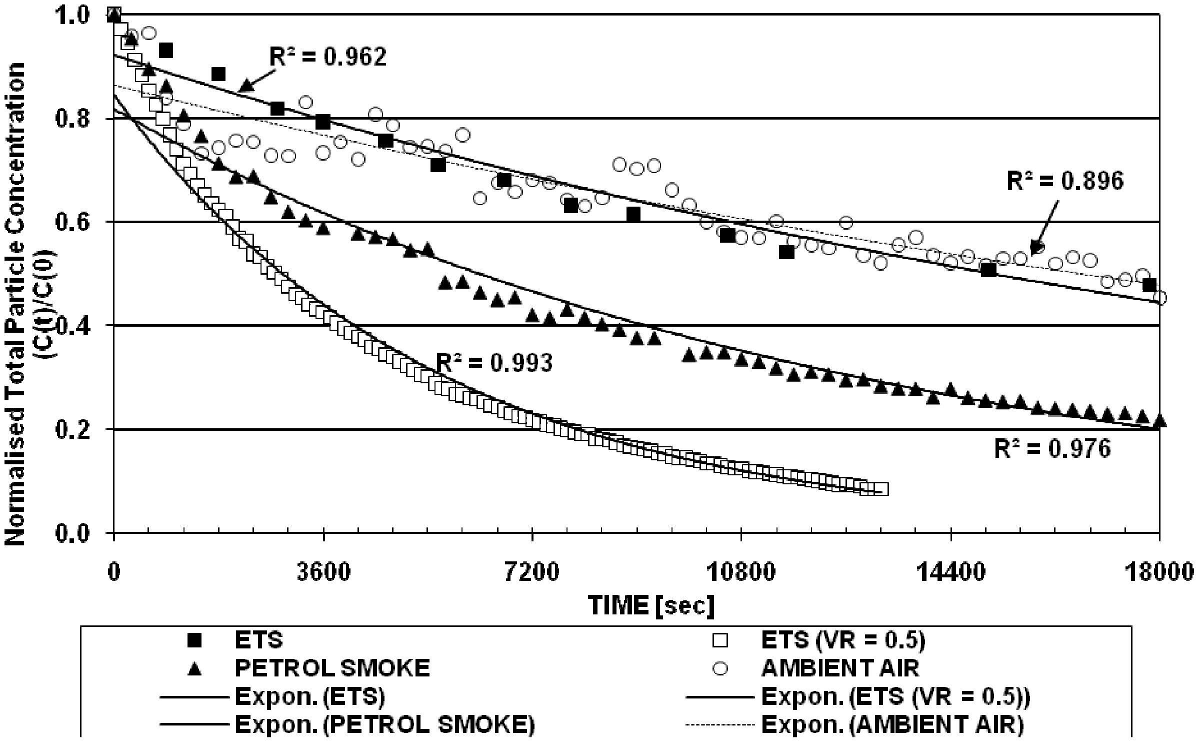

FIGURE 1 The evolution in total particle concentration for different test aerosols (normalised by *C(t=0)*).

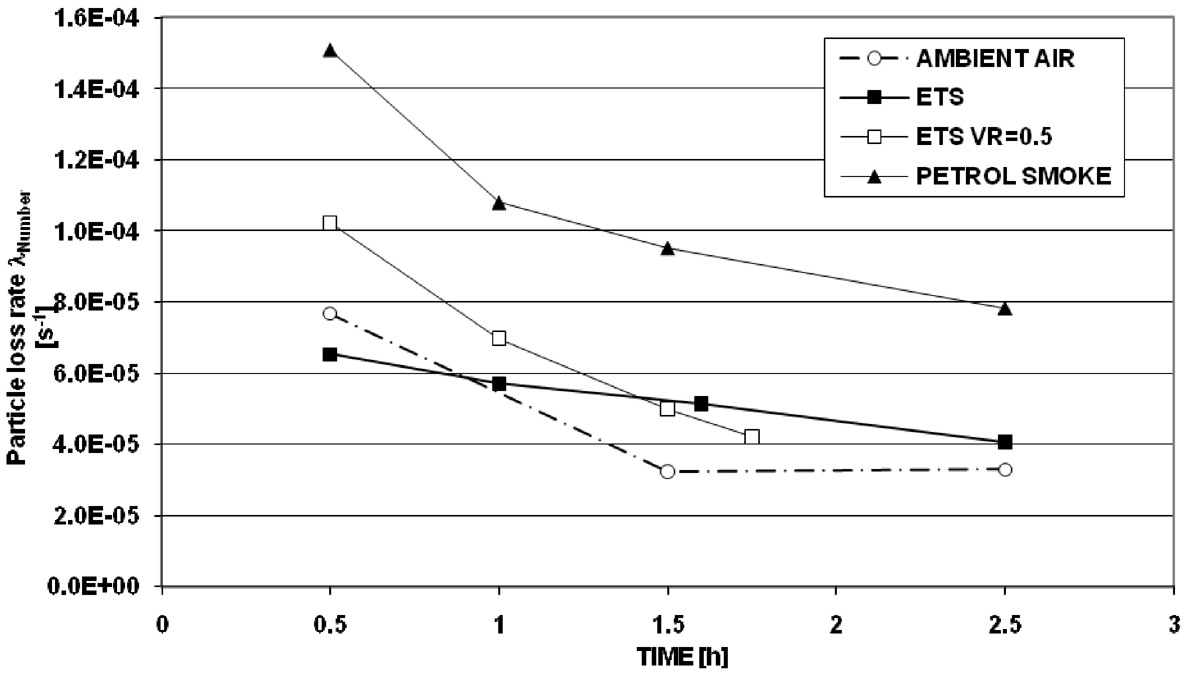

FIGURE 2 The overall particle loss rate (due to SD and CG) measured over different time intervals.

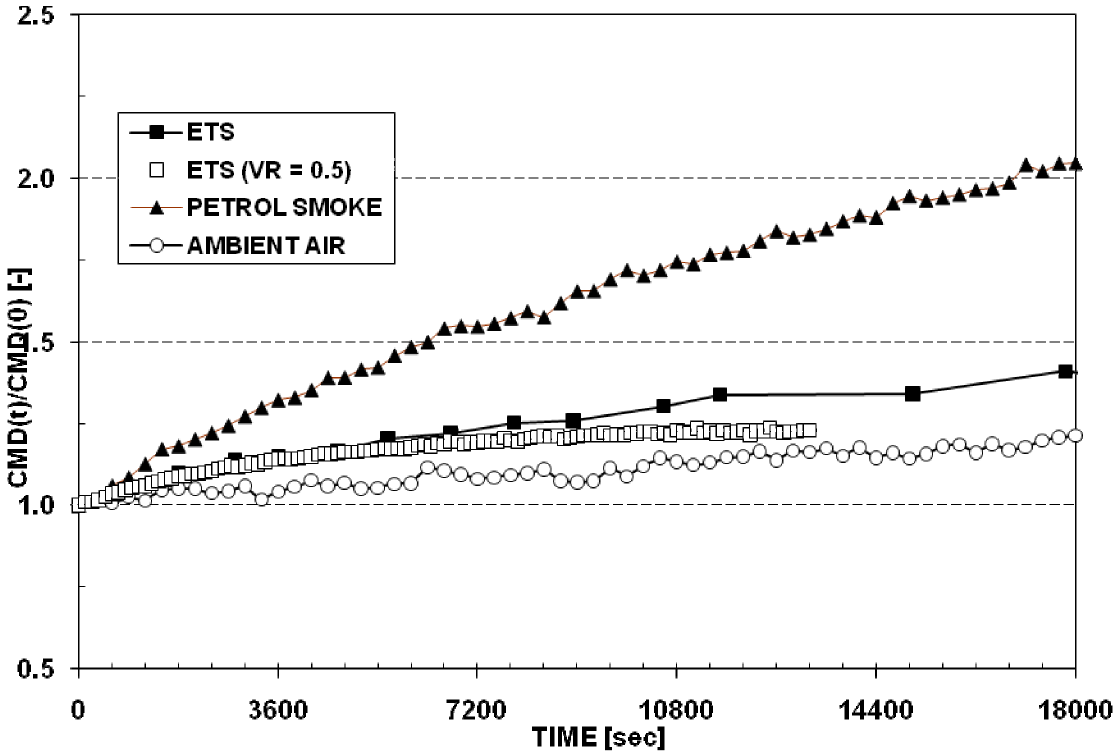

FIGURE 3 The evolution in CMD for different aerosols (normalised by *CMD(t=0)*).

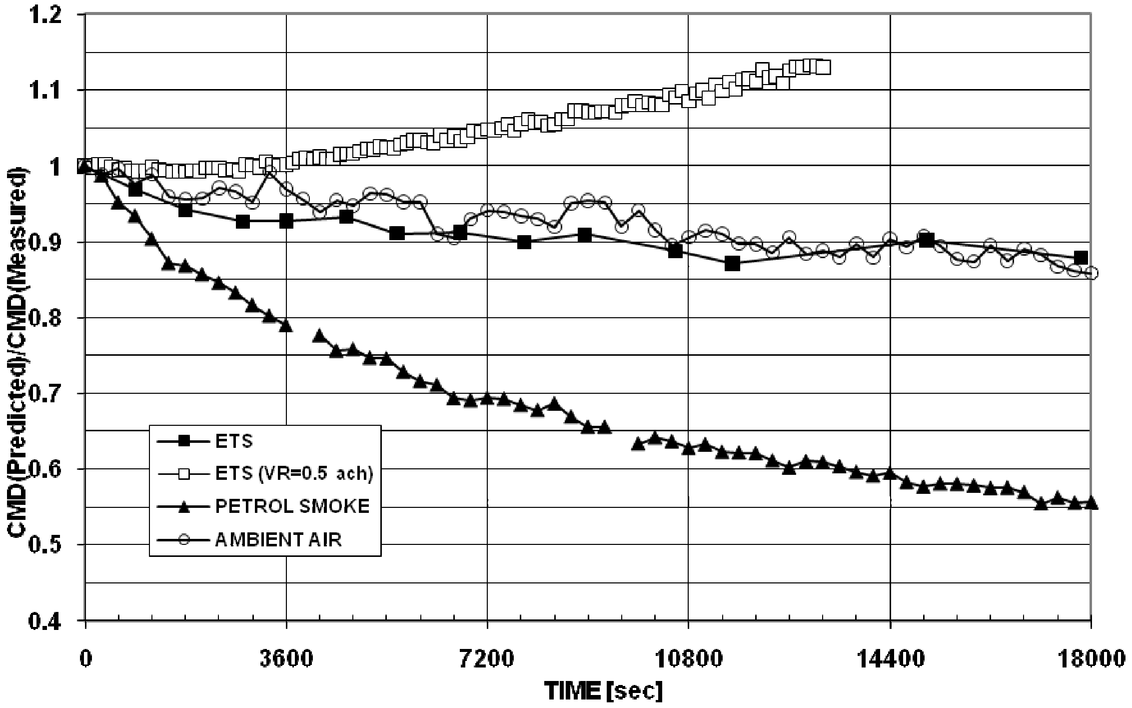

FIGURE 4 Ratio between predicted and measured count median diameter (CMD) for individual measurement runs (VR ~ 0 ach). The predicted values are based on changes effected by particle coagulation.

FIGURE 5 Relation between particle concentration and particle overall loss rate (SD + CG) measured over different time intervals.

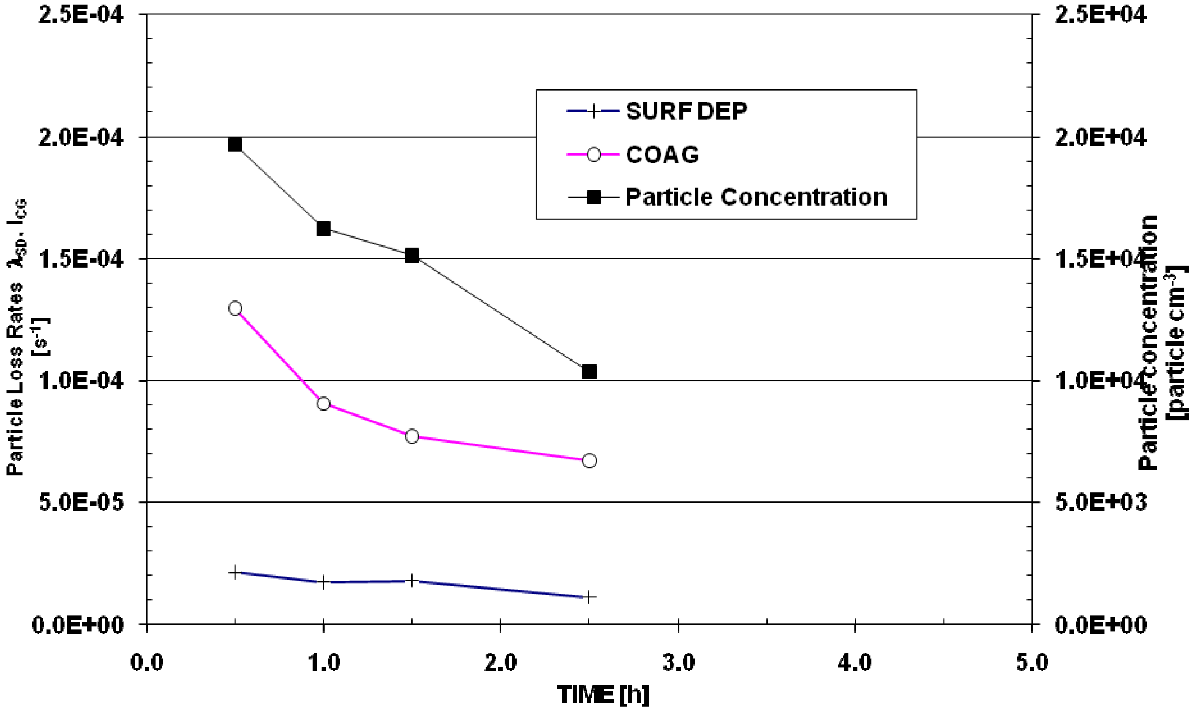

FIGURE 6 Particle loss rates due to SD and CG for Petrol smoke (VR=0 ach) measured over different time intervals.

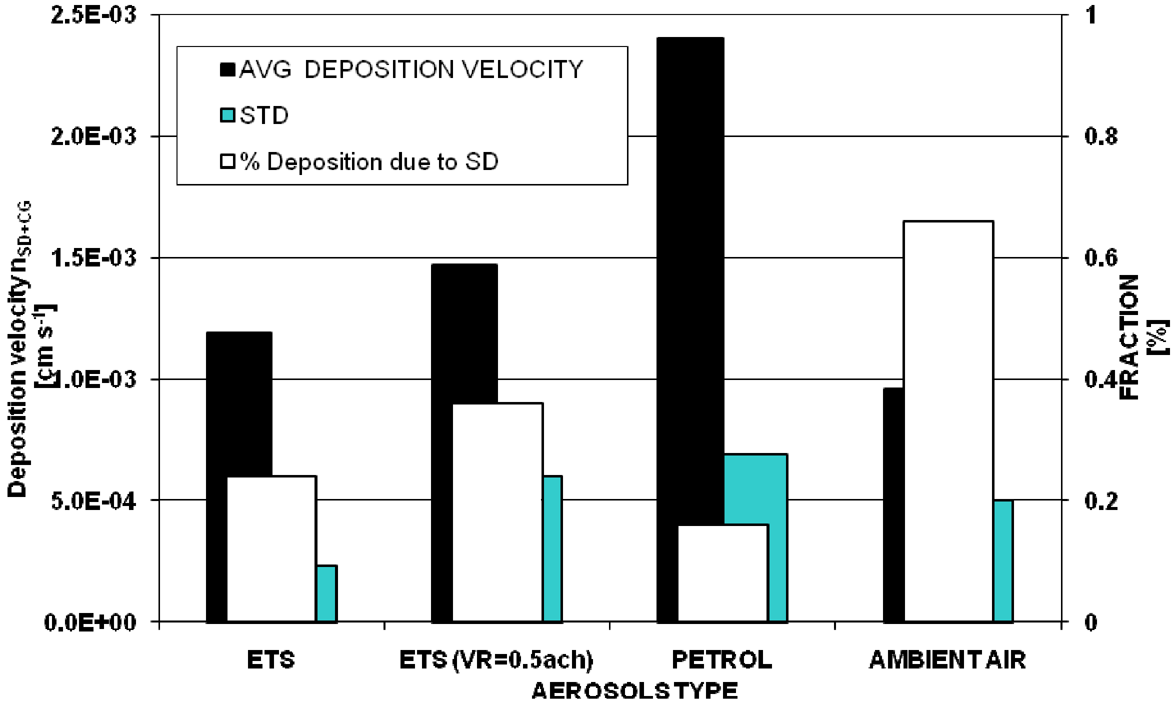

FIGURE 7 Measured deposition velocity v_{Number} (due to SD+CG) and the relative contribution of SD into overall particle losses.

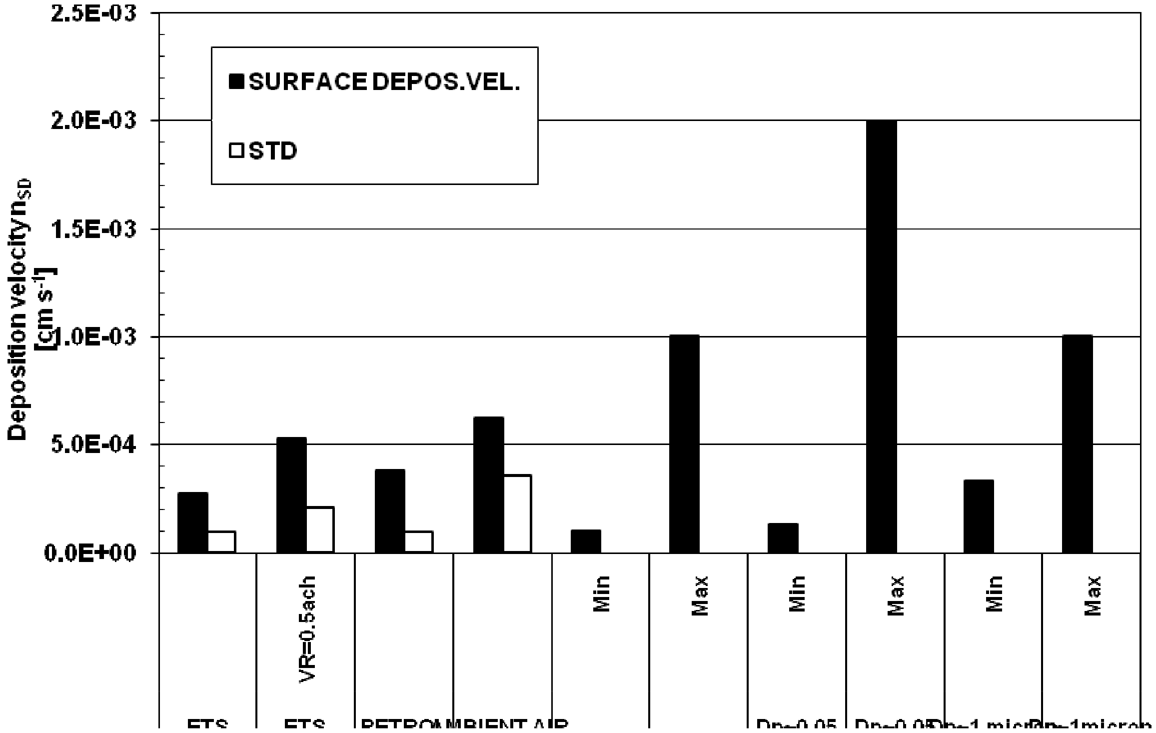

FIGURE 8 Review of measured and literature reported values of surface deposition velocities for submicrometer particles.

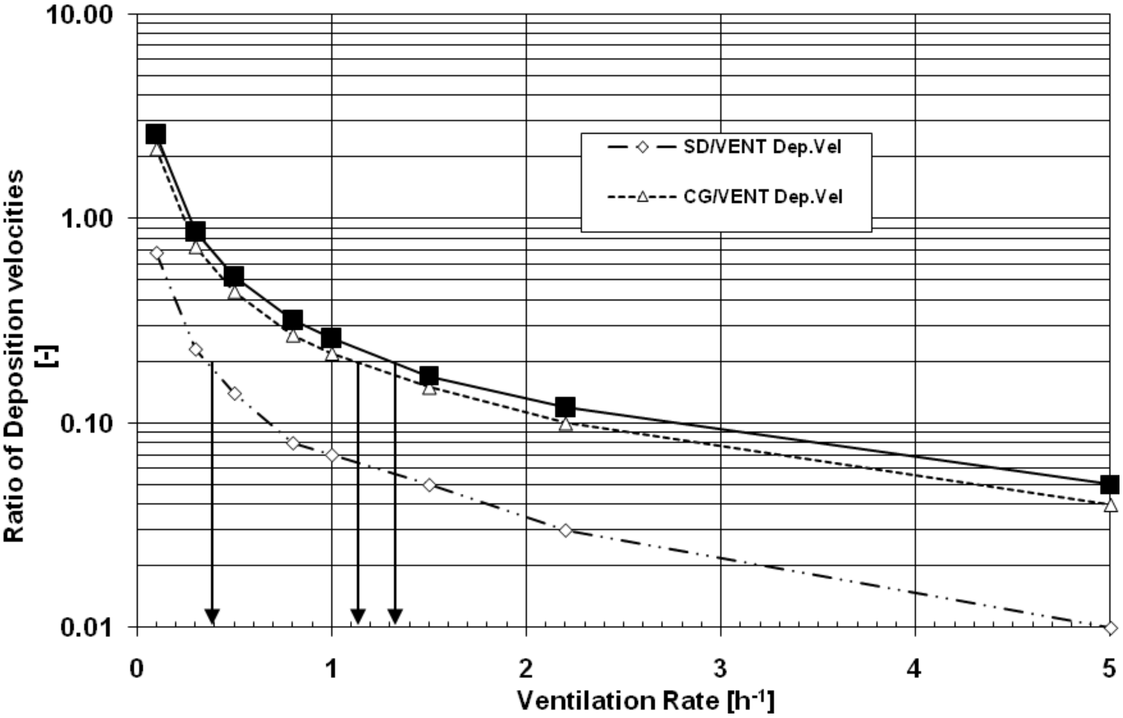

FIGURE 9 Assessment of the effect of surface deposition, coagulation and ventilation into the overall particle losses using the ratios of deposition velocities.

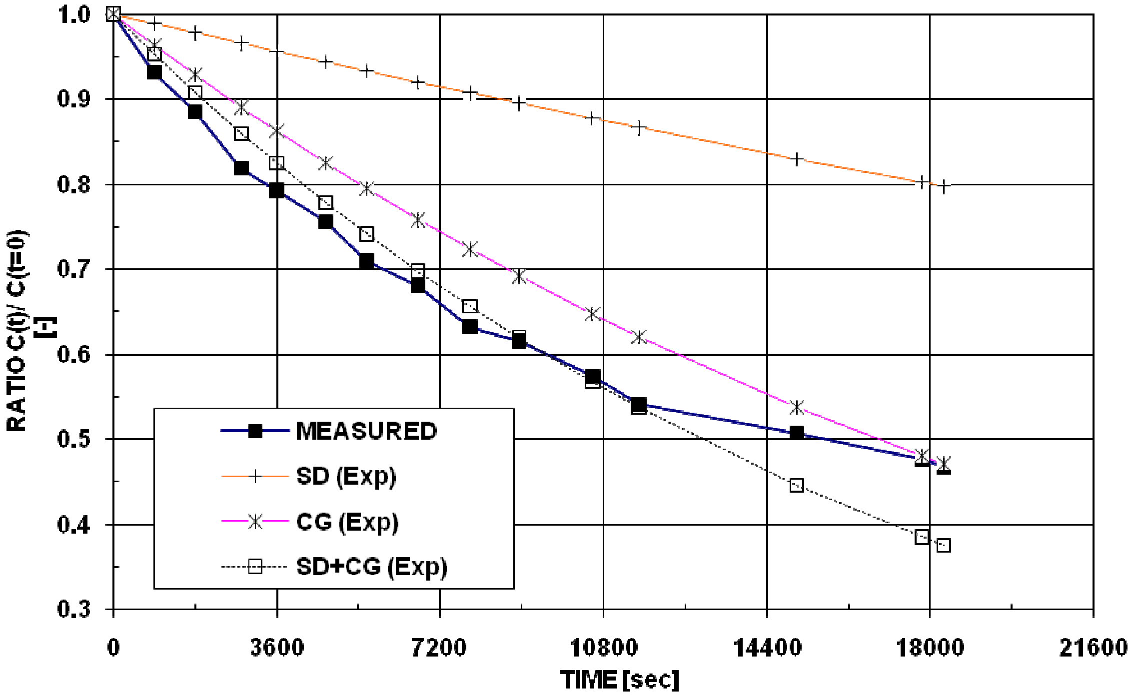

FIGURE 10 Ratios of measured vs predicted evolution in particle concentration (ETS, VR = 0 ach). The predicted values are based on experimentally determined values of deposition velocities for SD and CG mechanisms.

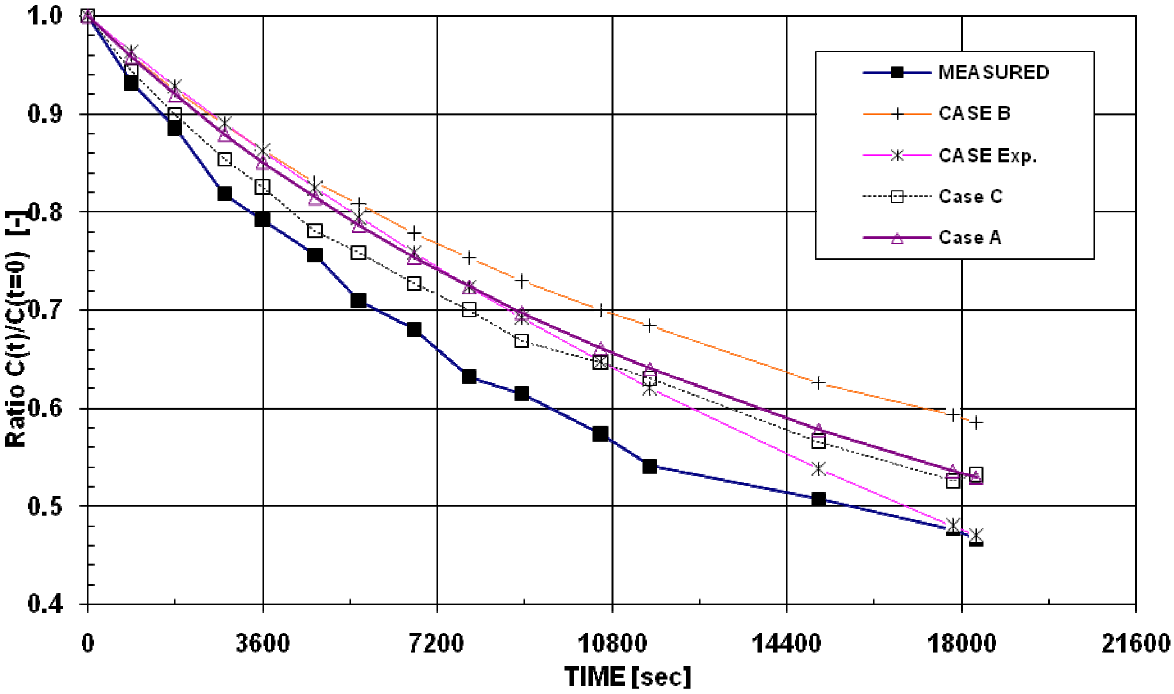

FIGURE 11 Ratios of measured vs predicted concentration (ETS, VR = 0 ach). Theoretically predicted values are based on various modes of coagulation (Case A , B, C) and measured loss rates associated with particle coagulation (Case Exp).

TABLES

Table 1 Initial characteristics of test aerosols and calculated average loss rates and deposition velocities.

TEST AEROSOL	INITIAL CHARACTERISTICS			SURFACE DEPOSITION and COAGULATION				FRACTION of PARTICLE DEPOSITION DUE TO		
	C(t=0)	CMD(t=0)	GSD (t=0)	LOSS RATE		DEPOSITION VELOCITY		SD	CG	STD
	[particle .cm^{-3}]	[μm]		λ_{SD+CG} [s^{-1}]	STD [s^{-1}]	ν_{SD+CG} [cm s^{-1}]	STD [cm s^{-1}]	ν_{SD} / ν_{SD+CG} [-]	ν_{CG}/ν_{SD+CG} [-]	[-]
ETS	5.91×10^{4}	0.108	1.8	5.35×10^{-5}	1.04×10^{-5}	1.19×10^{-3}	2.30×10^{-4}	0.24	0.76	0.06
ETS[*1)]	1.52×10^{5}	0.111	1.7	6.60×10^{-5}	2.68×10^{-5}	1.47×10^{-3}	6.00×10^{-4}	0.36	0.64	0.01
PETROL SMOKE	2.76×10^{4}	0.077	2	1.08×10^{-4}	3.10×10^{-5}	2.40×10^{-3}	6.90×10^{-4}	0.16	0.84	0.02
AMBIENT AIR	2.65×10^{3}	0.035	1.8	4.31×10^{-5}	2.25×10^{-5}	9.58×10^{-4}	4.99×10^{-4}	0.66	0.34	0.24

[*1)] VR=0.5 ach

TABLE 2 Comparison between deposition velocities corresponding to particle surface deposition, coagulation and ventilation mechanisms

VENTILATION		SURFACE DEPOSITION vs VENTILATION	COAGULATION vs VENTILATION	SURFACE DEPOSITION + COAGULATION vs VENTILATION
$\lambda_{vent}^{*1)}$ [h^{-1}]	$\nu_{vent}^{*2)}$ [$cm\ s^{-1}$]	ν_{SD}/ν_{vent}	ν_{CG}/ν_{vent}	ν_{CG+SD}/ν_{vent}
0.1	$9.26x10^{-6}$	0.68	2.19	2.59
0.3	$2.78x10^{-5}$	0.23	0.73	0.86
0.5	$4.63x10^{-5}$	0.14	0.44	0.52
0.8	$7.41x10^{-5}$	0.08	0.27	0.32
1.0	$9.26x10^{-5}$	0.07	0.22	0.26
1.5	$1.39x10^{-4}$	0.05	0.15	0.17
2.2	$2.04x10^{-4}$	0.03	0.10	0.12
$5.0^{*3)}$	$4.63x10^{-4}$	0.01	0.04	0.05

*1) Selected ventilation rates are based on the results of PTEAM and other studies presented by Wallace 1996.

*2) velocity corresponding to a ventilation rate: $\nu_{vent} = \lambda_{Vent}.V/S$.

*3) Hitchins, et al. 1999.

TABLE 3 The contribution of gravitation, diffusion and thermophoresis on particle surface deposition

		Overall Surface Deposition$^{*1)}$		Gravitational settling		Diffusional Deposition		Thermophoretic Deposition	
Measuring run$^{*2)}$	CMD(0) $[\mu m]$	$\lambda_{SD}^{*3)}$ $[s^{-1}]$	ν_{SD} $[cm\ s^{-1}]$	ν_{Grav} $[cm\ s^{-1}]$	ν_{Grav}/ν_{SD} [-]	ν_{Diff} $[cm\ s^{-1}]$	ν_{Diff}/ν_{SD} [-]	ν_{Therm} $[cm\ s^{-1}]$	ν_{Therm}/ν_{SD} [-]
ETS	0.108	$1.24x10^{-5}$	$2.75x10^{-4}$	$1.61x10^{-5}$	0.06	$6.98x10^{-5}$	0.25	$2.12x10^{-4}$	0.77
ETS VR = 0.5 ach	0.127	$2.38x10^{-5}$	$5.3x10^{-4}$	$1.99x10^{-5}$	0.04	$3.45x10^{-4}$	0.65	$2.05x10^{-4}$	0.39
PETROL SMOKE	0.077	$1.70x10^{-5}$	$3.78x10^{-4}$	$1.05x10^{-5}$	0.03	$1.73x10^{-4}$	0.46	$2.26x10^{-4}$	0.60
AMBIENT AIR	0.35	$2.82x10^{-5}$	$6.26x10^{-4}$	$4.24x10^{-6}$	0.01	$5.2x10^{-4}$	0.83	$1.54x10^{-4}$	0.25

$^{*1)}$ determined experimentally

$^{*2)}$ VR = 0 ach

$^{*3)}$ $\nu_{SD} = \nu_{Grav} + \nu_{Diff} + \nu_{Therm}$

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