Reply to Referee #2

We thank Referee #2 for critical comments to the manuscript. Following the Reviewer's remarks, a comprehensive evaluation of the uncertainties of the aerosol dynamic processes and of the dilution parameterization has been included in the revised manuscript.

1. ***Several fundamental assumptions seem to ignore processes that could make major qualitative differences in the results.***

   1.a. Given the relatively large contribution of diesels to the vehicle fleets, and in port cities such as Rotterdam, marine vessels their attendant fleet of lorries, the contribution from fractal agglomerates would seem to be much too high to ignore. Ignoring these particles and their very different behavior appears to be capable of introducing a significant error. The distribution data seem to imply significant contributions from diesel particles for some sites (such as Rotterdam) which have few very small particles. At the very least this the magnitude of the potential error from this omission should be estimated. Possibly differences between the sites could be used to better constrain MAFOR.

Response:

Model calculations for the idealized scenario assumed that all particles are spherical. Treatment of aggregates of soot as fractal particles increases the coagulation rate. The effect of fractal geometry on coagulation will be taken into account in the revised manuscript by considering the effect on radius, diffusion coefficient and the Knudsen number in the Brownian collision kernel, following the approach described by Jacobson and Seinfeld (2004).

For the treatment of fractal geometry of soot particles in MAFOR the coagulation kernel was modified by assuming that the collision radius is equal to the fractal (outer) radius, defined as:

$$r_{f,i} = r_s n_{s,i}^{1/D_f}$$

Where $n_s = \upsilon_i / \upsilon_s$ is the number of primary spherules in the soot aggregate, υ_i is the volume of the aggregate, treated as if it were spherical, r_s is the radius of spherules and υ_s is the volume of a spherule that makes up the aggregate, and D_f is the fractal dimension. Soot particle density was corrected as explained in Lemmetty et al. (2008).

The effect of fractal geometry of soot aggregates can only be of significance for those campaigns or locations where coagulation has been identified as an important process. Rotterdam showed the highest contribution of coagulation to PN losses under moderate dispersion conditions (see Table 4 of the original manuscript), but unfortunately particles with Dp < 10 nm have not been measured in that campaign. Due to the dominant contribution of dilution to PN losses at all sites, and the competition between coagulation and dry deposition with respect to the loss of nanoparticles (Dp < 25 nm), which made up the largest PN fraction at roadside (except at Rotterdam), it is not possible to better constrain the coagulation process in the model.

The description of the treatment of fractal geometry in MAFOR will be added in the new section 3.5 “Effect of fractal geometry of soot particles and van der Waals forces”.

1.b. Ignoring van der Waals forces leads to underestimation of coagulation rates that is of order a factor of two for the smaller particles (10s of nm). This will make a very substantial difference in the outcome of the calculations, and one that cannot be ignored.

Response:

The effect of van der Waals forces on coagulation is usually treated in combination with viscous forces (Jacobson and Seinfeld, 2004), which both affect primarily the small particles. Van der Waals forces are weak dipole-dipole attractions in uncharged, nonpolar molecules caused by random fluctuations in the electron cloud. Viscous forces are fluid mechanical interactions arising from the fact that velocity gradients induced by a particle approaching another particle in a viscous medium affect the motion of the other particle. Viscous forces retard the rate of van der Waals force enhancement in the continuum regime. It has been shown that van der Waals forces can enhance the coagulation rate of small particles by up to a factor of five (Jacobson and Seinfeld, 2004). However the degree of enhancement depends on the Hamaker constant A which is specific for the van der Waals properties of each substance. Jacobson and Seinfeld (2004) used a value of A/k_BT = 200 (k_B is the Boltzmann constant and T is the air temperature), which gave plausible enhancement for the coagulation of soot particles. However, for some values of the Hamaker constant there is an overall retardation of the coagulation rate in the continuum regime due to viscous forces. In the kinetic regime, coagulation is always enhanced due to the absence of viscous forces. The uncertainty related to the Hamaker constant was the reason for not including the effect of van der Waals forces in the original manuscript.

A simplified treatment of the van der Waals enhancement combined with retardation by viscous forces was considered sufficient to evaluate the possible uncertainty introduced into our study by neglecting the two interactions. A correction factor $V_{E,i,j}$ due to van der Waals and viscous forces was applied to the Brownian collision kernel in the MAFOR model:

$$K_{i,j}^{corr} = K_{i,j}^{B} \cdot V_{E,i,j}$$

Based on Fig. 3 in Jacobson and Seinfeld (2004), three regimes of enhancement were distinguished in the implementation, depending on the value of the particle pair Knudsen number, Kn_p, of two colliding particles with radius r_i and r_j:

$$Kn_p = \frac{\sqrt{\lambda_{p,i}^2 + \lambda_{p,j}^2}}{r_i + r_j}$$

Where λ_p is the effective mean free path of an individual particle.
The three cases for the correction factor are approximated by:

$$V_{E,i,j} = \begin{cases} 1.0 \quad , Kn_p < 0.1 \\ 2.0 + 0.4 \cdot \ln\left(Kn_p\right) \quad ,0.1 \le Kn_p \le 10.0 \\ 3.0 \quad , Kn_p > 10.0 \end{cases}$$

Clearly, $V_{Ei,j}$ for values of the particle pair Knudsen number greater than 1.0 depends on the radius ratio of the two colliding particles and can range from 1.0 to 5.0 for ratios between 50 and 1, when $A/k_BT = 200$ is used. A value (enhancement factor) of 3.0 was chosen which corresponds to a radius ratio of about 5, e.g. describing the collision of a 5 nm-particle with a 25 nm-particle, relevant for the studied size distributions at roadside. The applied correction value is higher than the factor of two suggested by the reviewer.

A brief description of the treatment of van der Waals forces and viscous interactions in MAFOR will be added in the new section 3.5 “Effect of fractal geometry of soot particles and van der Waals forces”. A detailed description is given in the new Supplement section S3 (“Modification of the Brownian coagulation kernel to approximate van der Waals forces and viscous interactions”).

> ***1.c The parameterizations and resulting rate estimates for dry deposition in the literature span more than an order of magnitude, and the calculations in this manuscript appear to be toward the high end. The manuscript would be much more useful and enlightening if it were to address this large source of uncertainty as well. Possibly the data again could be used to constrain dry deposition parameterization schemes. But at least this needs to be addressed directly as a source of uncertainty.***

Response:

Measurements of dry deposition velocities of particles for one particular surface type generally vary by approximately one order of magnitude for a given particle size range of a half logarithmic decade (e.g. for different grassland and forest types; Fig. 12 in Petroff et al., 2008). The typical mean measured deposition velocity values are within 0.1−1.0 cm s^{-1} for vegetated surfaces in the 0.1 and 1.0 µm particle size range (Zhang et al., 2001). Average dry deposition velocities were in the range of 0.2−0.9 cm s^{-1} in the studied campaigns for the reference case parameterization “KS2012 Urban”, well within the range reported by Zhang et al. (2001).

For size-dependent dry deposition velocities to typical urban surfaces: asphalt, roof bricks, concrete tile, and gravel only limited measurements exist. For these slightly rough surfaces, the measurement uncertainty is expected to be similar as for field measurements of vegetated surfaces (i.e. one order of magnitude) due to the difficulties of the measurements and different methods and assumptions during different measurement studies.

However, the span of literature values is smaller than the span between the upper line (“H2012, High Roughness”) and lower line (“H2012, Low Friction”) in our Figure 2 (size-dependent dry deposition velocity) which can be interpreted as the uncertainty range of tested dry deposition parameterizations.

The uncertainty due to available dry deposition measurements has to be distinguished from the uncertainty due to treating the underlying urban surface as homogeneous in the idealized scenario. The latter uncertainty can however be eliminated when the respective surface type is considered in the urban models, for example by using look-up tables of the size-dependent dry deposition velocity for each relevant surface (or land use) type.

Due to the dominant contribution of dilution to PN losses at all sites, and the competition between dry deposition and coagulation with respect to the loss of nanoparticles ($D_p < 25$ nm), which made up the largest PN fraction at roadside (except at Rotterdam), it is not possible to better constrain the dry deposition process in the model.

The following text will be added to the new section 3.6 ("Uncertainties of the aerosol treatment in the idealized scenario"):
"Measurements of dry deposition velocities of particles for one particular surface type generally vary by approximately one order of magnitude for a given particle size range of a half logarithmic decade (e.g. for different grassland and forest types; Petroff et al., 2008). Dry deposition velocities for total PN ($0.2-0.9$ cm s^{-1}), calculated with the reference case parameterization "KS2012 Urban", correspond to the reported range of measured deposition velocity values."

1.d The authors completely ignore additional emissions sources that happen between the roadside site and the "background" site. How does this effect the uncertainties on the estimates?

Response:

We have already clarified in our reply to the Comment by Prof. Roy M. Harrison and co-workers, that no additional emissions are collected during transport from roadside to ambient in the idealized scenario. Additional sources of ultrafine particles between the roadside site and the background site, i.e. downwind of the roadside, would also influence the particle size distribution that has been measured at the urban background site. In principle, particles emitted from additional sources on the travel path are integrated in the shape of the average size distribution of the urban background site. However, if there are strong emissions of ultrafine particles on the way, the momentary particle size distribution might strongly be changed resulting in somewhat different results at 3600 m distance than without extra emissions. However, since we don't have emission inventories available, the more accurate simulations could not be performed.

Figure 4 shows that the modeled particle size distribution converges with the measured size distribution at the urban background site after a distance of 3600 m from the roadside site under moderate dispersion conditions. Therefore momentary fluctuations in the dilution rate due to additional emissions during the travel path are expected to have a small effect on the effective total PN loss.

> ***Both the van der Waals and the diesel agglomerate issue have effects that goes in only one direction, and we know which direction that is. Further, it is possible to estimate (bracket) the size of most of the effects. In this situation, the authors need to address the size of the potential effects, and also include in their analysis the fact that both 1.a and 1.b skew the results in a single direction (unless fractal agglomerates behave like spheres and van der Waals forces do not exist, but there is abundant evidence to the contrary in both cases). The dry deposition uncertainty can go in either direction, but also results in large uncertainties. 1.d may be a smaller effect.***

Response:

The combination of the two effects, fractal geometry of soot aggregates (1.a), and van der Waals forces together with viscous interactions (1.b), substantially enhanced the loss of nanoparticles during advection of the exhaust plume from roadside to the neighborhood scale. The effect of fractal particles is now taken into account using the fractal parameters r_s = 13.5 nm and D_f = 1.7 given by Jacobson and Seinfeld (2004). In addition, fractal parameters from the study by Lemmetty et al. (2008), r_s = 2.5 nm and D_f =2.5, were also tested. Figure C1 shows how the consideration of van der Waals forces assuming either spherical or fractal geometry of aggregates enhances the coagulation kernel for the collision with a 10-nm particle (volume-equivalent diameter), as implemented in the MAFOR model. Figure C1 will be included as Figure S5 in the Supplement.

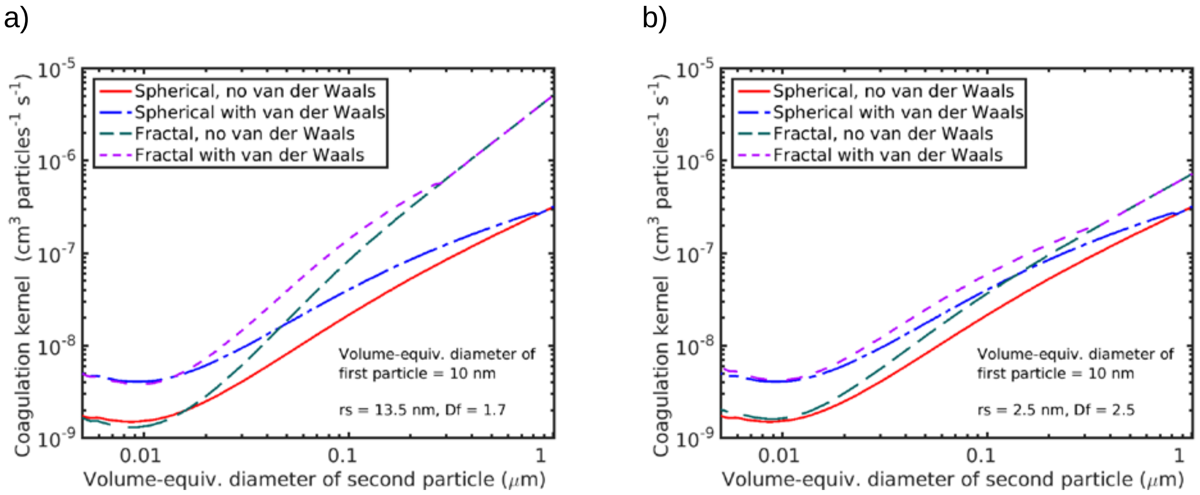

Figure C1: Brownian coagulation when the volume-equivalent diameter of the first particle is 10 nm and the volume-equivalent diameter of the second particle varies from 5 to 1000 nm: a) fractal geometry (rs = 13.5 nm, Df = 1.7) adapted from Jacobson and Seinfeld (2004), b) fractal geometry (rs = 2.5 nm, Df = 2.5) adapted from Lemmetty et al. (2008). The four curves account for when particles are spherical or fractal and when van der Waals and viscous forces (parameterized as described in section S3) are or are not included.

The size distribution of Helsinki MMEA was chosen to demonstrate the two effects in a scenario simulation since it was found that coagulation is a relevant process and a high fraction of nanoparticles was present at the roadside site. Coagulation contributed ca. 10% to PN losses after 600 m distance. Taking into account the fractal geometry as well as van der Waals and viscous forces doubled the contribution of coagulation to PN losses, resulting in a 15% higher loss of total PN compared to the reference simulation. Figure C2 shows how the modeled size distribution after 600 m distance from the roadside was affected by the two effects, assuming inefficient dispersion conditions. Figure C2 will be included as Figure S6 in the Supplement.

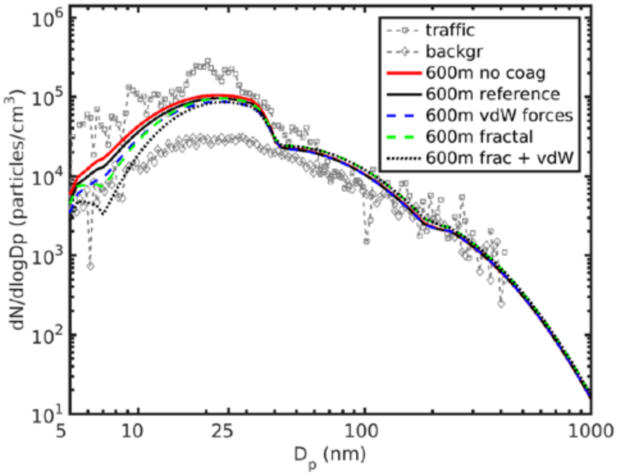

Figure C2: Sensitivity of the modeled size distribution to the effects of fractal geometry and van der Waals forces combined with viscous forces in campaign Helsinki-MMEA for inefficient dispersion. Modeled number size distributions (dN/dlogDp in particles cm^{-3}) 600 m downwind for reference case, i.e. spherical particles, coagulation by Brownian motion only (black line), case with coagulation of spherical particles enhanced by van der Waals and viscous forces (blue dashes), case with fractal geometry (green dashes) according to Jacobson and Seinfeld (2004), and case with coagulation of fractal particles enhanced by van der Waals and viscous forces (black dots). Red curve shows the modeled size distribution for the case without coagulation.

The uncertainty of coagulation by not considering fractal geometry (1.a) and by not considering van der Waals forces and viscous interactions (1.b) is addressed in our reply to point 3 of the reviewer.

The uncertainty due to the literature span of dry deposition values (1.c) was estimated in relation to the reference case by increasing and decreasing the “KS2012 Urban” deposition velocity by a factor 2 and 1/5, respectively.

The uncertainty due to additional emissions of particles on the travel path between the roadside site and the background site (1.d) was estimated in relation to the reference case by uniformly decreasing the dilution rate for all particles by 5%.

The following text with respect to point 1.a and point 1.b will be added in the new section 3.5 (“Effect of fractal geometry of soot particles and van der Waals forces”):
“The effect of van der Waals forces and viscous interactions as well as fractal geometry on the Brownian collision kernel is shown in Figure S5. Parameters of the fractal geometry adapted from Jacobson and Seinfeld (2004), r_s = 13.5 nm and D_f = 1.7, resulted in stronger enhancement of the coagulation rate for collisions with a 10 nm particle than the parameters (r_s = 2.5 nm and D_f = 2.5) adapted from Lemmetty et al. (2008).”

The following text with respect to the effect of point 1.a and point 1.b on the modelled size distributions will be added in the new section 3.5:
“The combination of both effects substantially enhanced the loss of nanoparticles in the simulation of the evolution of the roadside aerosol. For Helsinki MMEA, inefficient dispersion

conditions, the enhancement was similar for the two effects, separately, i.e. spherical particles with van der Waals and viscous forces versus fractal particles (Figure S6). The combined effect increased the loss of total PN by 15% compared to the reference simulation (coagulation of spherical particles by Brownian motion) in 600 m distance from the road."

2. ***All studies considering the effects of particle dynamics in emissions to the atmosphere struggle with the issue that dilution is responsible for the majority of the changes observed in particle concentrations and size distributions (see also comments from Prof. Harrison and co-workers). This means researchers are trying to tease out the small effects of coagulation/condensation/deposition (and evaporation?) when the vast majority of the aerosol evolution is caused by dilution, not any of the other processes.***

   2.a. First, the manuscript would be more clear if the contribution of dilution to the final concentrations was included explicitly.

Response:

The contribution of dilution to the final concentrations (after 30 min travel time) for each dispersion case will be included explicitly in Table 4.

2.b. The test applied to verify the MAFOR is working – start out with near roadway air, dilute with background air and arrive at the background concentration profiles needs to be tested for sensitivity to processes other than dilution, and to the dilution scheme as well. The bugger with this type of analysis is that the model needs to meet quite high standards to be able to verify parameterizations for dry deposition, condensation and coagulation. And even then, given the uncertainties for the minor processes, it is hard.

Response:

The primary goal of this study was to identify aerosol dynamic processes that are able to compete with dilution and to quantify the associated PN losses on the neighborhood scale. Validation of the MAFOR model was not intention of the study, despite the good agreement with the measured particle size distribution at the urban background sites. PN losses by dilution are overwhelming and the relatively small contribution from aerosol processes has to be carefully evaluated. Evaluation of different parameterizations of individual aerosol processes would only be possible with several intermediate sampling positions in 100-1000 m distance downwind between the roadside and the background site. However, the current study tried to include different urban settings, exhibiting different traffic conditions and different sampling periods, in order to arrive at a generally applicable simple parameterization for modelling PN concentrations in urban models.

Coagulation by Brownian motion is treated in a physical accurate manner in the model hence does not require verification in a field study. Different empirical parameterizations of size-dependent dry deposition rates, which were compared in the present study, show considerable spread, resulting in three different time scale estimates for use in the simplified parameterization. Condensation and evaporation are treated as physical process but important constraints such as measurements of gas-phase and particle-phase concentrations of semi-volatile and low-volatile compounds are lacking.

3. ***The estimates of all processes need well founded error bars, or at the very least a hard-headed discussion of uncertainties. This will go a long way to addressing comments 1. And 2. If done well, it will make the manuscript much better.***

Response:

We agree with the reviewer's suggestion to perform a rigorous analysis of uncertainties associated with each aerosol dynamic process, and also for the dilution parameterization applied in the idealized scenarios. This will help to highlight the need for more investigations of certain aerosol dynamic processes in future.

An uncertainty analysis was performed to quantify the errors associated with the determination of the contribution of the respective atmospheric processes to the change of total PN. Errors were determined based on simulations for the mean traffic-related particle distribution (obtained from a fit of MAFOR to the average of the size distribution curves for all traffic sites) under inefficient dispersion conditions after 30 min travel time. Figure C3 depicts the percentage contribution to total PN losses, together with the error bars for aerosol processes, additional emissions, and the dilution scheme. Figure C3 will be included as Figure 6 in the revised manuscript.

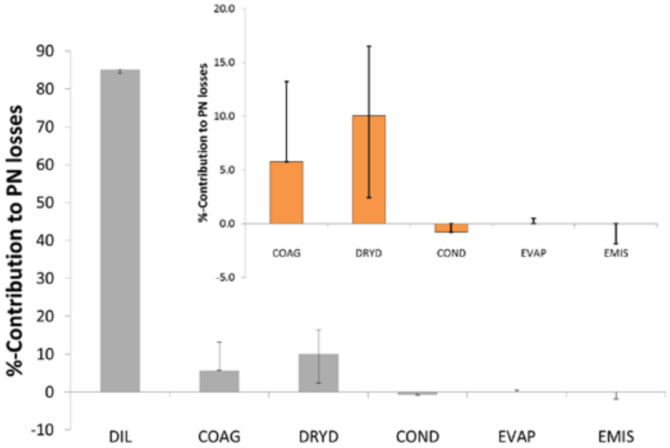

Figure C3: Contribution of processes to the percentage change of PN concentrations between roadside station and neighborhood environment, and their associated uncertainty depicted as error bars. Inset magnifies the contribution and uncertainty of the aerosol processes and additional emissions of particles.

The following sentences will be added to the new section 3.6 ("Uncertainties of the aerosol treatment in the idealized scenario").

With respect to coagulation:
“Fractal geometry parameters of Jacobson and Seinfeld (2004) were chosen for the evaluation of the uncertainty of the coagulation process. The combined effect of fractal geometry and van der Waals plus viscous interactions was taken into account, resulting in an error of +130%, roughly corresponding to a doubling of the contribution of coagulation to PN losses between roadside station and the neighborhood.”

With respect to dry deposition:
“Here, dry deposition velocity was scaled by factor 2 and 1/5 to evaluate the uncertainty of the dry deposition process due to literature span of measured velocities. This resulted in an error margin from -76% to +64% for the contribution from dry deposition.”

With respect to condensation and evaporation:
“For the mean traffic-related particle distribution, evaporation contributed 0.3 % to PN losses when assuming 0.005 ppb C22 + C28 and 100% C22 in <10 nm particles. Condensation and evaporation are uncertain processes due to the lack of measurements of the gas-phase and particle phase concentrations of condensable compounds at the roadside station. Oxidation of VOC from vehicular emissions may provide an additional source of condensable material on the neighborhood scale. However, oxidized VOC in the background air are expected to condense on the particles of the accumulation mode, increasing their volume, rather than changing PN concentrations.”

With respect to additional emissions:
“Additional emissions of particles on the travel path between the roadside station and the background were not considered in the idealized scenario. Since the dilution process in the model simulations was constrained with the measured size distribution at the background, the influence of additional particle emissions has been implicitly taken into account. However, if there are strong emission sources of ultrafine particles on the way, the momentary particle size distribution might be perturbed. The error due to fluctuations of the dilution rate caused by additional emissions was estimated to be -2 %.”

With respect to the dilution scheme:
“The main uncertain parameter in the applied dilution scheme [Eqs. (1) and (2)] is the initial plume height at the roadside, $H_{m,0}$. Doubling $H_{m,0}$ resulted in a small error (-1%) of the contribution of dilution to PN losses.”

4. ***P 35184 Given the uncertainties in coagulation resulting not just from not interacting size bins but also the assumptions in comment 1, the claim of dry deposition rates within 10% seems optimistic.***

Response:

The paragraph on page 35184 refers to the accuracy of the simplified PN parameterization as compared to the fully size-resolved aerosol dynamics and also to the potential improvements of the parameterization, not to the uncertainty of the modeled aerosol dynamic processes. The formulation in the original manuscript was ambiguous and will be corrected. Furthermore, concluding remarks from the uncertainty analysis of the aerosol dynamic processes (point 3) will be added to the Conclusions.

The sentence “The parameterization of aerosol processes can predict particle number concentrations between roadside and the urban background within an inaccuracy of 10%.” will be changed to “The parameterization of dry deposition and coagulation can predict total particle number concentrations between roadside and the urban background within an inaccuracy of 10%, compared to simulations with the fully size-resolved MAFOR model.”

The following text will be added to the Conclusions:
“Computation of the aerosol evolution between the roadside station and the neighborhood environment involved several assumptions and uncertain parameters. Due to the lack of measurements of the gas-phase and particle phase concentrations of semi-volatile compounds during the studied campaigns, the contributions from condensation and evaporation of condensable vapors emitted with the vehicle exhaust to PN changes are uncertain. Due to the wide span of measured deposition velocities in literature, the contribution from dry deposition to PN losses has an uncertainty range from -76% to +64%. The removal of nanoparticles by coagulation is further enhanced when considering the fractal nature of soot aggregates and the combined effect of van der Waals and viscous interactions. Taking into account these effects doubles the contribution of coagulation to PN losses between roadside and neighborhood.”

The following text will be added to the Abstract:
“The error of the contribution from dry deposition to PN losses due to the uncertainty of measured deposition velocities ranges from -76% to +64%. The removal of nanoparticles by coagulation enhanced considerably when considering the fractal nature of soot aggregates and the combined effect of van der Waals and viscous interactions”

References:

Jacobson, M. Z. and Seinfeld, J. H.: Evolution of nanoparticle size and mixing state near the point of emission, Atmos. Environ., 38, 1839-1850, 2004.

Lemmetty, M., Rönkkö, T., Virtanen, A., Keskinen, J., and Pirjola, L.: The effect of sulphur in diesel exhaust aerosol: Models compared with measurements, Aerosol Sci. Technol., 42, 916-929, 2008.

Petroff, A., Mailliat, A., Amielh, M., and Anselmet, F.: Aerosol dry deposition on vegetative canopies. Part II: A new modelling approach and applications, Atmos. Environ., 42, 3654-3683.

Zhang, L., Gong, S., Padro, J., and Barrie, L.: A size-segregated particle dry deposition scheme for an atmospheric aerosol module, Atmos. Environ., 35, 549-560, 2001.