6.2 PROCESSES AND PARAMETERS CONTROLLING MOTOR VEHICLE ULTRAFINE PARTICLE EMISSIONS: NUMERICAL SIMULATIONS AND COMPARISONS WITH OBSERVATIONS

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1. Introduction

Epidemiological studies have consistently linked urban fine particles (FPs, diameter less than or equal to 2.5 μm) to adverse health effects, including increased morbidity and mortality in people with respiratory and cardiac disease (e.g., Pope, 2000). A major source of fine particles in urban areas is the motor vehicle emissions (e.g., Shi et al., 2001). Present engine particulate emission standards are based on mass, and the EPA has proposed more stringent standards on ambient fine particles.

Recently it has been pointed out that it is not sufficient to study only the mass of fine particles (e.g., Wichmann and Peters, 2000). The main concern is that, while ultrafine particles (UPs, diameter less than or equal to 0.1 μm) contribute a small fraction to the mass concentration of the ambient aerosol, they may contribute disproportionately to its toxicity because of their high number concentration and surface area, high deposition efficiency in the pulmonary region, and high propensity to penetrate the epithelium (Donaldson et al., 2000). A recent comparison of the health effects of UPs with those of FPs indicates that UPs as well as FPs are associated with mortality (Wichmann et al., 2000). The other concern about the vehicle UP emissions is the indications that reductions in mass emissions of FPs may increase number emissions of UPs (e.g., Bagley et al., 1996; Kreso et al., 1998).

In view of the strong adverse health effects associated with UPs, future standards might be imposed on UP emissions and UP emissions from spark-ignition engines may also become a concern (Kittelson, 1998). Effective and least costly means of UP emission reduction must be based on a firm physical understanding of the processes and parameters controlling formation and evolution of ultrafine particles in vehicle exhaust. Such an understanding is also important to interpret the measurements taken under different conditions and to develop aerosol emission inventories which are important to study health, chemical, and climatic effects of aerosols.

2. UP formation mechanism in vehicle exhaust

Measurements of UPs in motor engine exhaust have been made both in the laboratory (e.g., Abdul-Khalek et al., 1999; Shi and Harrison, 1999) and in the atmosphere (e.g., Kittelson et al., 2000). The number concentrations of measured particles are typically dominated by nuclei mode particles (diameter ≤ 50 nm). In contrast to accumulation and coarse mode particles, nuclei mode particles are formed during exhaust dilution from low volatile precursor gases and the measured concentrations are very sensitive to dilution and sampling conditions (Abdul-Khalek et al., 1999; Shi and Harrison, 1999; Kittelson et al., 2000).

A mechanism of engine UP formation involving binary nucleation of H_2SO_4-H_2O followed by condensation growth of organic compounds has been proposed and supported by modeling of nucleation and growth combined with measurements of particle compositions (Shi and Harrison, 1999; Tobias et al., 2001) and particle growth rates (Abdul-Khalek et al., 2000). While organic compounds may contribute to the growth rate of newly formed particles, only sulfuric acid is likely to become super-saturated enough for homogeneous nucleation during dilution (Abdul-Khalek et al., 2000). Chen (1999) suggested that nucleation might also result from the chemicals vaporized from ambient aerosols in the intake air.

The classical H_2SO_4-H_2O binary homogeneous nucleation (BHN) theory of various versions has been applied to study the new particle formation in diluting diesel exhaust (Baumgard and Johnson, 1996; Shi and Harrison, 1999). It has been found that the BHN theory was not able to explain several key aspects of the observed properties of UPs (i.e., total concentrations, Shi and Harrison, 1999; sensitivity to FSCs, Abdul-Khalek et al., 1999, 2000). These discrepancies may suggest that mechanism other than BHN is responsible for UP formation. One of the possible mechanisms is ion-mediated nucleation (IMN) (Yu and Turco, 2000). Yu and Turco (2000, 2001) demonstrated that charged molecular clusters can grow significantly faster than corresponding neutral clusters, and thus can preferentially achieve stable, observable sizes.

A clear example of the strong influence electrification exercises on charged clusters and UPs has been demonstrated in aircraft wakes, where combustion chemiions (CIs) rapidly evolve into a distinct "ion-mode" of volatile particles (Yu and Turco, 1997). The CI theory predicts the complex behavior of

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aircraft aerosols (Yu et al., 1998, 1999; Kärcher et al., 1998), and is supported by measurements of massive ion clusters in fresh aircraft plumes (e.g., Arnold et al., 2000; Wohlfrom et al., 2000). In jet engine exhaust at the ground, Arnold et al. (2000) measured a positive CI concentration of ~1.6x10^8/cm^3 at a distance 1.39 m behind the engine and concluded that positive CI concentration at the exit plane was at least 1x10^9/cm^3.

We expect that vehicle engine exhaust also contains CIs, and the processes controlling particle formation in the exhaust are likely to be similar in most respects to those controlling aircraft aerosols. The upper limit values of CI concentrations at exit plane of motor vehicles are estimated to be in the range from 10^7 to 10^9 cm^{-3} (Yu, 2001).

3. UP formation in vehicle wake: Case studies

We have analyzed one specific experiment made on an engine test bed as reported by Shi and Harrison (1999). The sampling system consists of two dilution stages. Table 1 shows important parameters related to the experiment, and a comparison of number concentration of particles measured by scanning mobility particle sizer (SMPS) and total particles nucleated based on BHN theory (Shi and Harrison, 1999). The sulfuric acid partial pressure was calculated based on a FSC of 400 ppm and sulfur to sulfuric acid conversion fraction (S_c) of 4%. It is clear that the nucleation rate predicted based on BHN theory is much smaller (a factor of 55) than those measured. Furthermore, the prediction suggests more particles are formed in the second stage (3.8x10^4/cm^3) than in the first stage (1.9x10^5/7.9 = 2.4x10^4/cm^3). This is also inconsistent with the observations which indicate that the total measured UPs are insensitive to second stage dilution conditions (e.g., Shi and Harrison, 1999).

Table 1. Important parameters related to the experiment and a comparison of number concentrations of particles predicted and measured, as reported in Shi and Harrison (1999).

	first stage	second stage
dilution ratio	9.9	7.9
diluting air (RH, T)	60%, 295 K	5.4%, 295 K
exhaust temperature (K)	321	298
residence time (s)	1.6	0.2
p_{H_2O} (mmHg)	14.5	2.8
$p_{H_2SO_4}$ (mmHg)	3.8x10^{-5}	4.9x10^{-6}
formed nuclei based on BHN (#/cm^3)	1.9x10^5	3.8x10^4
predicted nuclei at measurement point (#/cm^3)		**6.2x10^4**
measured nuclei by SMPS(#/cm^3)		**3.4x10^6**

To investigate if IMN theory can explain the observed UP formation for the case reported by Shi and Harrison (1999), we employ an advanced particle microphysics model that simulates a size-resolved multi-component aerosol system via a unified collisional mechanism involving both neutral and charged particles down to molecular sizes (Yu and Turco, 2001). The model is constrained using the data in Table 1. Based on the measurements (e.g, Abdul-Khalek et al., 1999), we initialize the soot particles in rare exhaust as a log-normal size distributions with total number concentration of 1.25x10^7/cm^3, mean diameter of 60 nm, and standard deviation of 1.6. For the simulations shown below, $[ion]_0$ represents the concentration of CIs of each sign (positive or negative) in the rare exhaust just before first stage dilution.

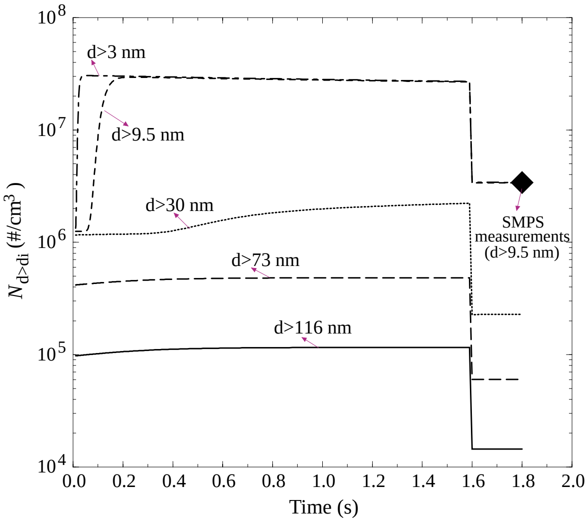

Figure 1. Predicted evolution of the total concentrations of condensation nuclei having diameter $d>d_i$ ($N_{d>di}$, d_i=3, 9.5, 30, 73, and 116 nm) in diesel exhaust. The measured UPs (d>9.5nm) at t=1.8 s by Shi and Harrison (1999) is also indicated. (From Yu, 2001)

Figure 1 describes the predicted evolution of the total concentrations of condensation nuclei (CN) having diameter $d>d_i$ ($N_{d>di}$, d_i=3, 9.5, 30, 73, and 116 nm) in diesel exhaust, assuming $[ion]_0$=1.5x10^8/cm^3. The CN measured with SMPS (d>9.5 nm) at t=1.8 s is also indicated. The simulations started immediately after first stage dilution that dilutes the concentrations of all species in the rare exhaust by a factor of 9.9. The drop of concentrations at t=1.6 s is due to second stage dilution. The second stage dilution appears to freeze out the microphysics processes at the time scale interested, which is consistent with observations that the measured total naoparticles are insensitive to second stage dilution conditions (e.g., Shi and Harrison, 1999). The simulated UP concentration based on IMN theory with $[ion]_0$ =1.5x10^8/cm^3 clearly reproduces the measured value at t=1.8 s.

Our simulations reveal that CIs are activated and new UPs (d>3 nm) begin to appear at t=~0.01 s, with $N_{d>3\ nm}$ increasing rapidly between 0.01 and 0.03 s and $N_{d>9.5\ nm}$ increasing rapidly between 0.06 and 0.2 s. Some of the newly formed particles have reached the size of 30 nm around t=0.5 s. Similar to volatile ultrafine particles formed in aircraft wakes (Yu and Turco, 1997), the volatile UPs formed in vehicle exhaust (not shown) also have a bimodal size distribution, in which an "ion-mode" constitutes the larger "activated" volatile sulfuric acid particles, while a mode of smaller neutral particles comprises the residual slowly-growing uncharged molecular clusters. Due to this bimodal structure of volatile particles size distribution, $N_{d>3\ nm}$ is stabilized after t>0.02 s, which indicates that most of ion-mode particles have grown to sizes larger than 3 nm by this time, while neutral mode particles remain smaller than 3 nm. Similarly, $N_{d>9.5\ nm}$ stabilizes after t>0.2 s. The small decrease (a few percentage) in $N_{d>3\ nm}$ and $N_{d>9.5\ nm}$ after reaching their maximum concentrations is due to self-coagulation and scavenging by soot particles.

4. Key parameters controlling UP formation

(1) Fuel sulfur contents

Nationally, on-road fuels averaged 0.032% sulfur (or 320 ppm) in 1994 while nonroad fuels averaged 10-fold the sulfur level of on-road fuel, or 0.32% (Dickson and Sturm, 1994). Most of the sulfur in the fuel is oxidized to SO_2, but a small amount (1% to 4%) is oxidized to SO_3 which rapidly forms sulfuric acid in the presence of water vapor in the exhaust. Sulfuric acid emissions are roughly proportional to FSCs. Since sulfuric acid is known to participate in the UP formation, it is of obvious interesting to study how FSC will affect UP emissions.

Based on classical BHN theory and THN theory, the formation rate (and hence the concentration) of UPs should be very sensitive to FSCs. However, Abdul-Khalek et al. (1999, 2000) found that the use of low sulfur fuel with FSC of 19 ppm (~40 ppm if the sulfur in lube oil was taken into account) led to reductions of only ~50% in total number concentrations compared to the 400 ppm sulfur fuel. We have carried out some preliminary simulations to see if this weak dependence of observed UP concentrations on FSCs can be explained by IMN theory.

With the case presented in Figure 1 (FSC=400 ppm) as baseline case, Figure 2 shows the ratio of total particles (d>3nm) formed in the cases for FSC=200 ppm and 40 ppm to that in baseline case, i.e., N^{200}/N^{400}, N^{40}/N^{400}, respectively. The observed N^{40}/N^{400} by Abdul-Khalek et al. (1999, 2000) is also indicated for comparison. The ratios are unity at t<0.008 s because all particles are soot particles which are same for different FSCs. The significant decrease in the ratios between 0.01 s and 0.02 s is due to new particle formation in baseline case (Figure 2). N^{200}/N^{400} increases between 0.03 s and 0.08 s as new UPs are formed in 200 ppm case while total UPs in baseline case have reached maximum concentration and stabilized. N^{200}/N^{400} stabilizes at t>0.08 s when all particles nucleated on CIs are bigger than 3 nm. Similarly, N^{40}/N^{400} increases between 0.15 s and 0.4 s and stabilizes thereafter.

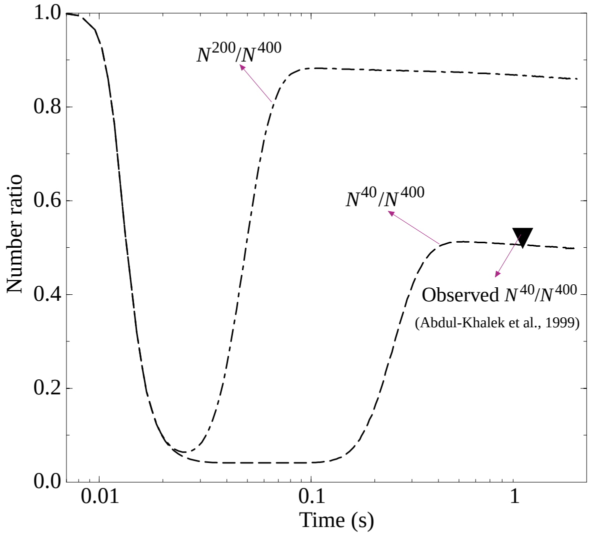

Figure 2. The ratio of total particles (d>3nm) formed in the cases for FSC=200 ppm and 40 ppm to that in baseline case (FSC=400 ppm), i.e., N^{200}/N^{400} and N^{40}/N^{400}. The observed value of N^{40}/N^{400} *by Abdul-Khalek et al.* (1999, 2000) is also indicated. (From Yu, 2001)

Under the conditions assumed, a reduction of FSC by a factor of 2 only reduces $N_{d>3\ nm}$ by 14%, and a reduction of FSC by a factor of 10 only reduces $N_{d>3\ nm}$ by 50% at measurement point (t=1.8 s). This predicted dependence of UP emissions on fuel sulfur content based on IMN theory is consistent with the measurements of Abdul-Khalek et al. (1999, 2000). The reason for this "unexpected weak" sensitivity of measured UPs to FSC (Abdul-Khalek et al., 1999, 2000) is that nucleated UPs in diesel exhaust are limited by the CI abundance. Due to high $[H_2SO_4]$ in the vehicle exhaust (~ $10^{11}/cm^3$ after first stage dilution for FSC=40 ppm with S_c=4%), most of CIs that survived recombination and scavenging are activated and become nucleated particles. Under the condition, the homogenous nucleation was negligible compared to the ion nucleation. The reduction in FSC (and thus $[H_2SO_4]_0$) reduces the growth rate of ions and thus increases the time needed for growing the ions to "nucleated" particles. Since ion-ion recombination coefficients and ion-soot coagulation kernels decrease significantly as the mass (or size) of ion increases (Yu and Turco, 2001), the relative longer time of CIs at smaller mass in lower FSC cases increases the recombination and soot scavenging loss of the ions. Therefore, the number of CIs survived recombination and scavenging is smaller in lower FSC case.

(2) Initial CI concentrations

Our preliminary studies indicate that CIs may play an important role in UP formation. No direct measurement of ions in vehicle engine exhaust has been reported (to our knowledge). We estimate that the upper limit value of the initial CI concentrations in the rare exhaust just before dilution (i.e., $[ion]_0$) could be in the range from 10^7 to 10^9 cm^{-3}. The actual concentration is likely to vary with different exhaust systems, engine types and operation conditions. It is necessary to study how sensitive is UP emissions to $[ion]_0$. Again we have carried out some preliminary simulations for the case (Shi and Harison, 1999) we have analyzed

Figure 3 shows the dependence of predicted concentrations of UPs (d>9.5 nm) on $[ion]_0$. All the parameters are same as that of Figure 2 except that we vary $[ion]_0$ from $10^6/cm^3$ to $10^9/cm^3$. Due to high $[H_2SO_4]$, the particles formed on CIs approach the size of 9.5 nm in less than 0.1 s and all are bigger than 9.5 nm by 0.2 s. The distinct plateau shape of the curves between 0.2 s and 1.6 s is a result of insignificant coagulation scavenging and absence of new particle formation after 0.2 s. The number of UPs at measurement point is very sensitive to $[ion]_0$ because the nucleation rate is limited by CI abundance under the conditions assumed.

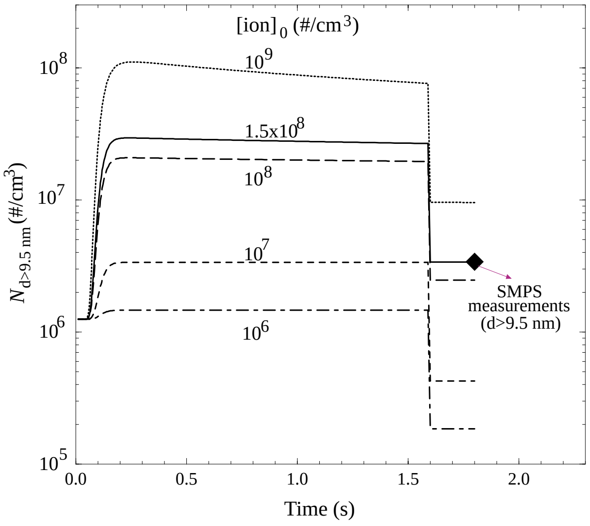

Figure 3. Predicted evolution of nanoparticle concentrations (d>9.5 nm) assuming different initial CI concentrations in the undiluted exhaust just before dilution (i.e., $[ion]_0$). (From Yu, 2001)

(3) Dilution conditions

Our preliminary study indicates that the dilution conditions (dilution ratio, temperature, relative humidity) influence the diesel UP production rate by affecting the precursor concentration, the interaction rate and stability of pre-nucleated clusters.

(4) Soot particle concentrations

Soot particles in the exhaust tend to suppress the formation and growth of nanoparticles by scavenging the precursor gases and newly formed UPs. Soot particles also affect $[ion]_0$ by scavenging them inside the tailpipe.

(5) Condensable organic compounds

Abdul-Khalek et al. (2000) concluded that organic compound absorbing into nucleated sulfuric acid particles must play a role in their growth since there is not enough sulfuric acid vapor in the exhaust to explain the observed growth rate. Chemical analysis of the ~30-73 nm diesel particles collected with an electrical low-pressure impactor showed that sulfuric acid mass fraction of these particles is only ~ 6% (Shi and Harrison, 1999). The chemical compositions of diesel engine UPs (mass median diameter ~25-60 nm) have been recently analyzed using a nano-DMA/thermal desorption particle beam mass spectrometer (Tobias et al., 2001). Branched alkanes and alkyl-substituted cycloalkanes from unburned fuel and/or lubricating oil appear to contribute most of these diesel nanoparticle mass, and sulfuric acid was detected at estimated concentrations of a few percent of the total mass (Tobias et al., 2001). Tobias et al. (2001) also found the volatility of the organic fraction of the aerosol increases as particle size increases.

Our preliminary study indicates the growth rate and mass of newly formed ultrafine particles are very sensitive to the vapor pressure, condensation accommodation coefficient, and concentration of the organic compounds.

5. Implications: UP emission control strategies

Present engine particulate emission standards are based on mass. Future standards on number (or UP) emissions may be enforced if UP emissions are found to be important. The least costly means of UP emission control strategies can only be identified based on a firm physical understanding of the UP formation mechanism. Since the sulfuric acid is known to participate in the UP formation, one logical control approach is to reduce the sulfur in the fuel. However, our study (supported by measurements, see Figure 2) indicate that reductions in fuel sulfur content, while can reduce the growth rate of initial charged clusters, are not likely to be very effective in reducing the total number of volatile particles formed unless sulfur content in the fuel (and lube oil) is extreme low. Since the cost of further decreasing FSC increases dramatically as the FSC decreases, we need to choose the FSC level on a cost-effective way. The effectiveness of FSC reduction on the growth rate and mass of UPs may also be limited by the condensation of organics on nucleated particles (Abdul-Khalek et al., 2000). Of course, FSC reduction will reduce SO_2 emission and the implication of such reduction to the associated environmental problems is out of the scope of this study.

The success of our IMN theory in explaining the observed UP properties in diesel exhaust suggest that CIs may play an important role in UP formation. Based on the strong dependence of emitted UP concentration on $[\text{ion}]_0$, we propose a technique to reduce the vehicle UP number emissions by removing ions in the rare exhaust. As shown in Figure 3, the volatile UP emission becomes insignificant compared to soot emission when $[\text{ion}]_0 < 10^6/\text{cm}^3$. The ions in the exhaust can be removed by imposing an electric field in the tailpipe. Figure 4 shows a schematic drawing of such a technique. In order to remove the ions, the electronic potential U to be imposed can be estimated based on

$$U = \frac{d^2 V}{ML}$$

where M is ion electric mobility and v is the velocity of exhaust inside the tailpipe. d is tailpipe diameter or the maximum distance between two ion collecting plates. L is the length of the portion of tailpipe where the electronic potential U is imposed. The mobility of ions increases with decreasing ion mass, and is proportional to temperature at constant pressure (for ions in free molecule regime). Measurements made at a pressure of 1 atm and temperature of 473 K (Kilpatrick, 1971) gave an M value of 4.09 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ for ions with mass of 46 amu and 1.57 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ for ions with mass of 500 amu. For typical exhaust inside the tailpipe with a temperature of ~ 600 K and pressure of 1 atm (Kittelson, 2001), M is ~5 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ for 46 amu ions and is ~ 2 $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ for 500 amu ions. Assuming d=0.1 m, V=5 m/s, and L= 1 m, we estimate that U=100 V for 46 amu ions and 250 V for 500 amu ions.

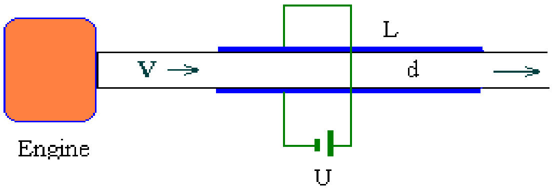

Figure 4. A conceptual and schematic drawing of a technique to control vehicle nanoparticle emissions by removing ions in the rare exhaust.

Note that the voltage U needed is very sensitive to d ($U \propto d^2$). Thus, we can effectively reduce U by reducing d. The values of d can be effectively reduced by applying multiple parallel chemiion collecting plates alternately connected to positive and negative poles of the car battery (or other suitable DC power sources) to keep a potential difference between two neighboring plates. By using 4 plates instead of 2 plates, the distance between two neighboring plates (d) is reduced by a factor of 3 and the voltage U needed is reduced by a factor 9. If v and L remain same (i.e., v=5 m/s and L= 1 m), the voltage U needed to remove 46 amu ions is only ~ 11 V and to remove 500 amu ions is ~ 28 V. The voltage U needed to remove chemiions will vary as v, d, L, and M change, and clearly there exists a trade-off between the voltage needed and the number of collecting plates. The optimum voltage and number of collecting plates needed can readily be determined through proper test.

6. Summary and Discussion

The adverse health effect associated with ultrafine particles (UPs) appears to become an emerging environmental problem, and it is important to understand the processes and parameters controlling motor vehicle UP emissions. Measurements of UPs in motor engine exhaust have been made both in the laboratory and in the atmosphere under various conditions. Most of UPs are formed during exhaust dilution from low volatile precursor gases and the measured concentrations are very sensitive to dilution and sampling conditions. In this study, we investigate the key processes and parameters controlling formation and evolution of UPs in vehicle exhaust through model simulations and comparisons with field measurements. The detailed aerosol dynamics (nucleation, condensation, and coagulation) are simulated with an advanced multi-type, multi-component, size-resolved microphysics model.

We find that chemiions generated in engine combustor may play an important role in the formation of UPs in vehicle exhaust. The predicted UP properties based on our ion-mediated nucleation of H_2SO_4-H_2O closely match measurements in terms of total UP concentrations, and their sensitivity to fuel sulfur contents and second stage dilution. Besides chemiion concentration and fuel sulfur content, other parameters affecting UP emissions include dilution conditions (temperature and humidity of diluting air, dilution ratio), soot particle concentration, and vapor pressure and concentration of condensable organic species.

Our study indicates that the number of UPs at measurement point is very sensitive to initial chemiion concentrations, and we propose a potentially effective technique to control vehicle UP emissions by imposing an electrical field on a section of the tailpipe to remove ions in the rare exhaust. The voltage needed to remove chemiions is estimated to be ~ 100-250 volts if the Chemiion Collector composed of two collecting plates and to be ~ 11-28 volts if the Chemiion Collector composed of four parallel collecting plates. The reductions in fuel sulfur content, while can reduce the growth rate (and size) of initial charged clusters, are not likely to be very effective in reducing the total number of volatile particles formed since the nucleation rate is limited by the CI abundance.

While no direct measurements of ions in vehicle engine exhaust are available (to our knowledge), we believe that the CIs generated during the combustion process should be present in the exhaust. The chemiion concentration needed to explain the observations seems to lie within the range of values we estimate. Obviously, direct measurements of CIs in vehicle exhaust are needed to confirm the proposed CI mechanism. Actually, based on our simulation, most of the fresh volatile UPs in diesel exhaust are formed on CIs and a significant fraction of these particles are still charged at plume age of ~ 1 s. Since SMPS is commonly used to measure the size distribution of UPs, a convenient way to test the chemiion theory is to measure the particles with ion neutralizer in SMPS turned off. On the other hand, the UPs measured with SMPS may have to be reassessed if a significant fraction of these particles are originally charged.

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