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Chemiions and nanoparticle formation in diesel engine exhaust

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Abstract. The nanoparticles (diameter < 50 nm) emitted by diesel engines have received increasing attention due to their potential health effects. We propose that chemiions generated during combustion play an important role in the formation of these nanoparticles. The predicted nanoparticle properties based on our chemiion theory closely match measurements in terms of total nanoparticle concentrations, and their sensitivity to fuel sulfur contents and second stage dilution conditions, while the classical homogeneous nucleation fails to explain these observed properties. Our study indicates that total number of nanoparticles formed is very sensitive to chemiion concentrations, and we propose a technique to effectively reduce vehicle nanoparticle emissions by removing ions in the exhaust.

Introduction

Concerns about the engine nanoparticle (NP; particles with diameter smaller than 50 nm) emissions are growing [*Kittelson*, 1998], mainly as a result of suggestions that a decrease in particle sizes increases its toxicity [e.g., *Donaldson et al.,* 1998] and indications that reductions in mass emissions may increase number emissions of NPs [*Bagley et al.,* 1996]. Diesel engines are known to contribute substantially to ambient concentrations of particulate matter. Often more than 90% (number) of NPs emitted by diesel engines are formed from precursors during exhaust dilution, and the measured number concentrations are very sensitive to dilution and sampling conditions [*Kittelson*, 1998; *Abdul-Khalek et al.,* 1999; *Shi and Harrison*, 1999; *Kittelson et al.*, 2000]. A clear physical understanding of how nuclei-mode particles are formed and evolve during exhaust dilution is of significant importance to interpret the measurements taken under different conditions and to design effective control strategies.

Based on measurements of the size-segregated particle compositions [*Shi and Harrison,* 1999] and particle growth rates [*Abdul-Khalek et al.,* 2000], a mechanism of diesel NP formation involving binary nucleation of H_2SO_4-H_2O followed by condensation growth of hydrocarbon has been proposed [*Shi and Harrison,* 1999, *Abdul-Khalek et al.,* 2000]. This mechanism is further supported by recent chemical composition analysis of diesel engine NPs [*Tobias et al.,* 2001]. While hydrocarbon may contribute significantly to the growth rate of nucleated 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 cooling and diluting diesel exhaust [*Baumgard and Johnson*, 1996; *Shi and Harrison,* 1999; *Abdul-Khalek et al.,* 2000]. While these theoretical analyses demonstrate that binary nucleation of H_2SO_4-H_2O can occur during dilution, one well constrained case study [*Shi and Harrison,* 1999] suggests that the predicted nucleation rates, based on the most recent thermodynamically correct hydration theory, are much lower than those measured. Furthermore, the weak dependence of observed NP concentrations on fuel sulfur contents (FSCs, in ppm by mass) is inconsistent with the high sensitivity of predicted binary nucleation rate on FSCs. For example, *Abdul-Khalek et al.* [1999, 2000] were surprised to find that the use of low sulfur fuel with FSC of 19 ppm (~40 ppm if the sulfur in lubrication oil was taken into account) led to reductions of only ~50% in total number concentrations compared to the 400 ppm sulfur fuel.

These discrepancies between predicted and observed behavior of NPs may indicate that mechanism other than BHN is responsible for NP formation. One possible mechanism is ion-mediated nucleation (IMN) involving ions and H_2SO_4-H_2O [*Yu and Turco*, 2000]. *Yu and Turco* [2000, 2001] demonstrate that charged molecular clusters, condensing around natural air ions, 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 NPs 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 IMN theory predicts the complex behavior of aircraft aerosols [e.g., *Yu et al.*, 1999], and is supported by measurements of CIs in fresh plumes [e.g., *Arnold et al.*, 2000]. We argue here that diesel engine exhaust also contains CIs (more discussion in the next section), and the processes controlling particle formation in diesel engine exhaust may be similar in most respects to those controlling aircraft aerosols. In this paper we study if the observed properties of diesel NPs are consistent with IMN theory.

Chemiions in engine exhaust

It is well known that chemiionization in hydrocarbon flames generates copious ions and electrons, and ion concentrations of up to 10^{10}-10^{11}/cm^3 have been reported [see review by *Fialkov, 1997*]. The charge concentration falls off quickly with increasing distance from the combustion source due to ion-ion recombination. In jet engine exhaust at the ground, *Arnold et al.* [2000] measured a positive CI concentration of ~1.6×10^8/cm^3 at a distance 1.39 m behind the engine and concluded that positive CI concentration at the exit plane was at least 1×10^9/cm^3.

To our knowledge, no direct measurement of ions in vehicle engine exhaust has been reported. We believe that large amount of CIs are produced in the vehicle engine combustor, as combustion chemistry is similar. The concentration of CIs at exit plane is controlled by the ion-ion recombination, wall loss, and soot particle scavenging in the tailpipe, and may also be affected by the exhaust aftertreatment devices (such as catalytic converter or filter). The upper limit of CI concentration at the exit plane can be roughly estimated based on ion-ion recombination coefficient (β_i)

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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)	3.8×10^{-5}	4.9×10^{-6}
formed nuclei based on BHN (#/cm^3)	1.9×10^5	3.8×10^4
predicted nuclei at measurement point (#/cm^3)		6.2×10^4
measured nuclei by SMPS (#/cm^3)		3.4×10^6

and the travel time of exhaust in the pipe before dilution. According to the review article by *Fialkov* [1997], for the hydrocarbon flame close to stoichiometry, the reasonable value of β_r is $2.4\pm0.4\times10^{-7}$cm^3/s. However, β_r can drop down to 10^{-8} cm^3/s when the flame becomes fuel-rich and then sooting, and further down to 3×10^{-9} cm^3/s when some additives of small amount are introduced [*Fialkov*, 1997]. Based on the nature of the diesel fuel and burning conditions, β_r in diesel exhaust (before dilution) may be ~ 10^{-8} cm^3/s or smaller. Under typical highway cruise conditions for a diesel truck, the exhaust leaves the tailpipe at a temperature of ~ 600 K and exhaust age (τ) of ~ 0.5 s [*Kittelson*, 2001]. In a sampling system at laboratory engine test bed, the exhaust age before dilution may be smaller. Based on the possible values of β_r and τ, we estimate that the upper limit values of CI concentration at the exit plane ($\approx 1/\beta_r\tau$) could be in the range from 10^7 to 10^9/cm^3.

Chemiions and NP Formation: Case Study

Measurements of NPs in diesel 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*, 2000]. Here we focus on one specific measurement carried out 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 maximum nucleation rate predicted based on BHN theory is much smaller (a factor of 55) than those measured [*Shi and Harrison,* 1999]. Furthermore, the prediction suggests more particles are formed in the second stage (3.8×10^4/cm^3) than in the first stage ($1.9\times10^5/7.9 = 2.4\times10^4$/cm^3). This is also inconsistent with the observations which indicate that the total measured NPs are insensitive to second stage dilution conditions [e.g., *Shi and Harrison,* 1999].

To investigate if IMN theory can explain the observed NP formation in diesel exhaust, 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 undiluted exhaust (i.e., exhaust in the tailpipe before emission or mixing with ambient air) as a log-normal size distributions with total number concentration of 1.25×10^7/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 undilued exhaust just before first stage dilution. The contribution of hydrocarbon to the growth of newly formed particles is not considered in this study.

Figure 1 describes the predicted evolution of the total concentrations of particles having diameter $d>d_i$ ($N_{d>di}$, d_i=3, 9.5, 30, 73, and 116 nm) in diesel exhaust, assuming $[ion]_0=1.5\times10^8$/cm^3. The particles 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 undiluted 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 NPs are insensitive to second stage dilution conditions [e.g., *Shi and Harrison,* 1999]. The simulated NP concentration based on IMN theory with $[ion]_0=1.5\times10^8$/cm^3 clearly reproduces the measured value at t=1.8 s.

Our simulations reveal that CIs are activated and new NPs (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 NPs 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 (here represented by d>3 nm), 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

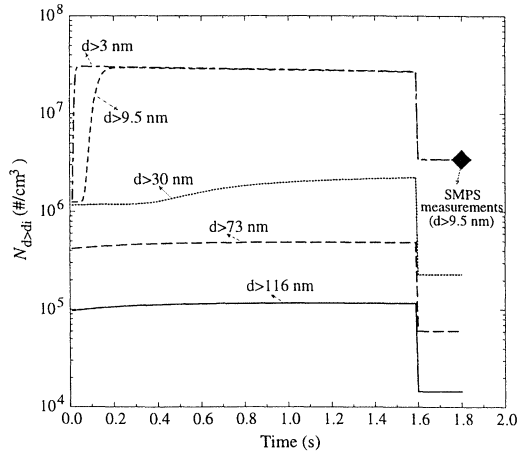

Figure 1. Predicted evolution of the total concentrations of condensation nuclei having diameter $d>d_i$ ($N_{d>di}$, d_i=3, 9.5, 30, 73, and 116 nm) in diesel exhaust, assuming $[ion]_0=1.5\times10^8$/cm^3. The measured nanoparticles (d>9.5 nm) at t=1.8 s by *Shi and Harrison* [1999] is also indicated.

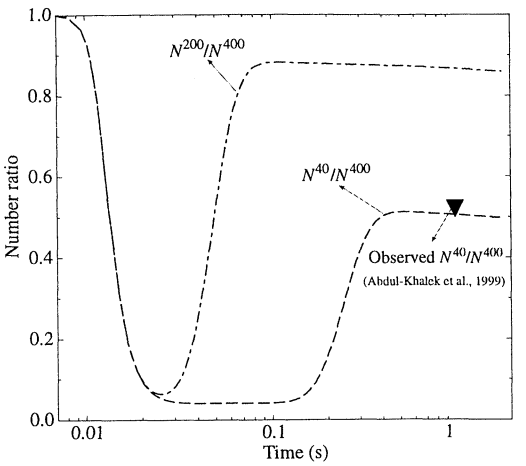

Figure 2. The ratio of total particles (d>3nm) formed in the cases for FSC=200 ppm and 40 ppm to that in baseline case (FSC=400 ppm), i.e., N^{200}/N^{400} and N^{40}/N^{400}. The observed value of N^{40}/N^{400} by *Abdul-Khalek et al.* [1999, 2000] is also indicated.

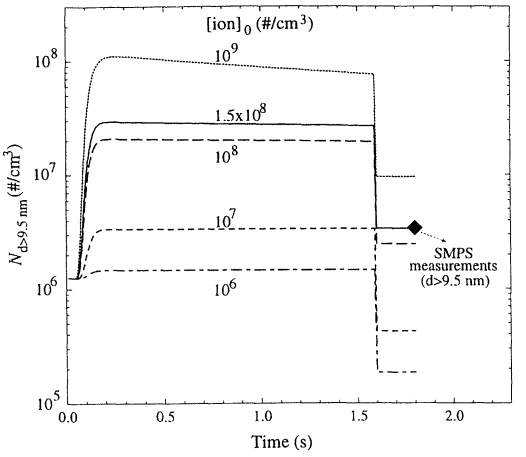

Figure 3. Predicted evolution of nanoparticle concentrations (d>9.5 nm) assuming different initial CI concentrations in the undiluted exhaust just before dilution (i.e., $[ion]_0$).

(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.

Sensitivity Studies and Implications

Sensitivity to fuel sulfur contents: 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}). S_c=4% is assumed in all cases. 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 1). N^{200}/N^{400} increases between 0.03 s and 0.08 s as new NPs are formed in 200 ppm case while total NPs 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.

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 NP 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 "surprising weak" sensitivity of measured NPs to FSCs [*Abdul-Khalek et al.*, 1999, 2000] is that nucleated NPs in diesel exhaust are limited by the CI abundance. Due to high $[H_2SO_4]$ in the 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.

We should note that the predicted curves in Figure 2 are for particles bigger than 3 nm while the measurements of *Abdul-Khalek et al.* [1999, 2000] are for particles bigger than ~8 nm. Due to the condensation of organics species [*Abdul-Khalek et al.*, 2000], it is likely that most of the nucleated particles in low FSC cases are bigger than 8 nm at the measurement point. While the growth rate of new particles will change if the condensation of hydrocarbon is considered, the total number of formed NPs is unlikely to change as long as the hydrocarbon is not involved in the particle nucleation.

Sensitivity to initial CI concentrations: The dependence of predicted concentrations of NP (d>9.5 nm) on the initial CI concentrations in the undiluted exhaust (i.e., $[ion]_0$) is illustrated in Figure 3. All the parameters are the same as that of Figure 1 except 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 NPs at measurement point is very sensitive to $[ion]_0$ because the nucleation rate is limited by CI abundance under the conditions assumed. It is expected that $[ion]_0$ varies with exhaust systems and engine operation conditions, and such variety may have contributed to the differences in the total NPs observed under various situations.

Sensitivity to dilution conditions: Our primary study indicates that the first stage dilution conditions (dilution ratio, temperature, relative humidity) influence the diesel NP production rate by affecting the concentrations of precursor gases, and the growth rate, stability and lifetime of pre-nucleated clusters. Systematic investigations will be carried out in the future.

Implications for NP emission control strategies: Present engine particulate emission standards are based on mass. This may have

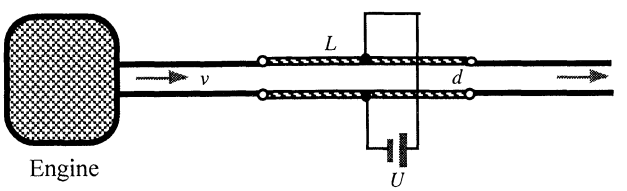

Figure 4. A schematic illustration of a technique to control vehicle nanoparticle emissions by removing ions in the exhaust.

to change if NP emissions are found to be important [*Kittelson*, 1998]. The success of our IMN theory in explaining the observed NP properties in diesel exhaust suggest that CIs may play an important role in NP formation. Based on the strong dependence of emitted NP concentration on $[ion]_0$, we propose a technique to reduce the vehicle NP number emissions by removing ions in the undiluted exhaust. As shown in Figure 3, the volatile NP emission becomes insignificant compared to soot emission when $[ion]_0 < 10^6/cm^3$. The ions in the exhaust can be removed by imposing an electric field on the tailpipe. Figure 4 shows a schematic illustration of such a technique. In order to remove the ions, the electric 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 electric potential U is imposed on. The mobility of ions increases with decreasing ion mass. For typical exhaust inside the tailpipe, M is found to be ~5 $cm^2V^{-1}s^{-1}$ for 46 amu ions and ~ 2 $cm^2V^{-1}s^{-1}$ 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. Note that U can be much smaller if multiple parallel collecting plates are applied to reduce d ($U \propto d^2$).

Summary and Discussion

Measurements of NPs in diesel exhaust have been made both in the laboratory and in the atmosphere. The classical H_2SO_4-H_2O binary homogeneous nucleation theory was not able to explain several key aspects of the observed properties of NPs (i.e., total concentrations, sensitivity to FSCs, and sensitivity to second stage dilution conditions). Here we demonstrate that CIs produced in the engine combustor may play an important role in the formation of new particles in the cooling and diluting diesel exhaust. Our simulations considering the role of CIs lead to aerosol properties that closely match measurements in terms of total NP concentrations, and their sensitivity to FSCs and second stage dilution conditions. 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 CI concentration needed to explain the observations seems to lie within the range of values we estimate. The NP formation mechanism proposed here may also apply to spike-ignition engines and other sources of combustion emissions.

We find that the number of NPs at measurement point is very sensitive to ion concentration in the undiluted exhaust just before dilution. Based on this new discovery of the relationship between CIs in undiluted exhaust and nanoparticle formation in engine wake, we propose a potentially effective technique to control vehicle NP emissions by removing ions in the exhaust using electrical fields. The reductions in fuel sulfur content (from a few hundreds ppm to a few tens ppm), while they can reduce SO_2 emission, the growth rate of initial charged clusters and mass of formed particles, 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.

Obviously, much more work (both experimental and theoretical) is needed to confirm the proposed vehicle NP formation mechanism and to study if the proposed technique to reduce NP emissions is practical. Here we suggest several approaches that could be carried out to verify the theoretical studies presented in this paper. First, measurements of chemiions and massive charged clusters in motor vehicle wake, as have been done in aircraft wake [e.g., *Arnold et al.*, 2000], would provide direct evidence supporting the NP formation mechanism. Second, the proposed mechanisms can be tested by measuring the changes in NP formed in the exhaust wake as the undiluted exhaust is passed through two spaced apart plane electrodes kept at different voltages. Third, based on our simulation, most of the fresh volatile NPs in diesel exhaust are formed on chemiions 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 NPs, a convenient way to test the chemiion theory is to see if a significant number of nanoparticles can still be measured when the ion neutralizer in SMPS is turned off.

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