Chemiion evolution in motor vehicle exhaust: Further evidence of its role in nanoparticle formation

Fangqun Yu

Atmospheric Sciences Research Center, State University of New York, Albany, New York, USA

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[1] The evolution of engine-generated chemiions in a vehicle tailpipe or in a sampling transfer line is studied and the key parameters controlling chemiion concentration at the exit plane are investigated. We find that the observed higher number concentration but smaller size of nuclei mode particles associated with shorter transfer line residence time, enhanced nanoparticle emission associated with reduced soot emission, and increase in the number concentration but decrease in the size of nuclei mode particles associated with increasing traffic speed, can all be consistently explained by the reduced loss of ions in the transfer line or tailpipe. This provides further evidence that engine-generated chemiions play a key role in the formation of the nanoparticles in motor vehicle exhaust. *INDEX TERMS:* 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305)

1. Introduction

[2] In view of the potential adverse health effects associated with nuclei mode particles or nanoparticles (NPs, diameter $\leq$ 50 nm) [e.g., *Seaton et al.*, 1995], future standards might be imposed on NP emissions and NP emissions from gasoline engines may also become a concern [*Kittelson*, 1998]. Effective means of NP emission reduction must be based on a firm physical understanding of the formation mechanisms of NPs in vehicle exhaust. Recently, *Yu* [2001] proposed that chemiions (CIs) generated during fuel combustion play an important role in the formation of these NPs. The predicted NP properties based on the chemiion (CI) theory closely match measurements which the homogenous nucleation theory fails to explain. *Yu* [2001] found that total number of NPs formed in motor vehicle exhaust is very sensitive to CI concentrations. The purpose of this paper is to investigate the key parameters controlling the evolution of CIs in a vehicle tailpipe or experimental sampling transfer line. The impacts of transfer line residence time, soot concentration, and vehicular speed on observed NP concentrations are then interpreted in term of their impacts on exiting CI concentrations.

2. Chemiions: Observations and Reasoning

[3] It is well known that in hydrocarbon flames chemiionization generates copious positive ions and electrons via reactions such as $CH + O \rightarrow CHO^+ + e$. The electrons rapidly attach to molecules to form primary negative CIs. Subsequently, both positive and negative CIs may react with certain molecules to form more stable charged clusters. Positive ion concentrations of up to 10^{10}–10^{11}/cm^3 have been reported in hydrocarbon flames [e.g., *Fialkov*, 1997]. The CIs are removed mainly by ion-ion recombination.

[4] Arguing that jet engine should also produce high concentration of CIs, *Yu and Turco* [1997] showed for the first time that these CIs might play a key role in the formation of volatile particles observed in aircraft wake. *Yu and Turco* [1997] also suggested that CI concentration should be controlled by ion-ion recombination and estimated that CI concentration at engine exit should be around 10^9/cm^3. This reasoning has been confirmed by measurements taken by *Arnold et al.* [2000], who detected a positive CI concentration of $\sim 1.6 \times 10^8$/cm^3 at a distance 1.39 m behind the jet engine and concluded that positive CI concentration at the exit plane should be at least 1×10^9/cm^3.

[5] We believe that large amount of CIs are produced in the motor engine, as combustion chemistry and process are similar to that in a jet engine [*Yu*, 2001]. The presence of ions in hydrocarbon flames had earlier lead *Kittelson et al.* [1986] to suggest that CIs should also be formed in a diesel engine. This suggestion has been supported by the measurements showing that diesel soot particles are highly symmetrically charged ($\sim$80% of particulate mass) [e.g., *Kittelson and Collings*, 1987]. *Kittelson et al.* [1986] mentioned that the ions generated in diesel engine are largely depleted by the end of the expansion stroke but didn't discuss how and how much these ions are depleted. Our calculation (shown below in section "Analytical results") indicates that ion concentration at the end of the expansion stroke should be $\sim 10^9$/cm^3. This value is much lower than the reported peak concentration of 10^{10}–10^{11}/cm^3 in hydrocarbon flames but is high enough to explain the observed volatile particles assumed to be formed on these ions [*Yu*, 2001].

3. Evolution of Chemiions Inside the Vehicle Tailpipe or Sampling Transfer Line – Analytical Solution

[6] The CI concentration at tailpipe and transfer line exit plane is controlled by ion-ion recombination, wall loss, and soot particle scavenging inside the tailpipe or sampling transfer line. Assuming same properties of positive and negative ions, we have

$$\frac{d[ion]}{dt} = -K_r[ion]^2 - \frac{[ion]}{\tau_s} - \frac{[ion]}{\tau_w} = -K_r[ion]^2 - \frac{[ion]}{\tau} \quad (1)$$

where $[ion]$ is the concentration of positive or negative ions, and K_r is the mean ion-ion recombination coefficient. τ is

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the combined characteristic time constant for soot scavenging (τ_s) and wall loss (τ_w) of ions. τ_s is equal to $1/(K_sN_s)$ where K_s is the average collection rate of ions by soot particles and N_s is the number concentration of soot particles.

[7] For the laboratory study we will analyze below, the exhaust flow in the transfer line is laminar [*Wei et al.*, 2001]. Following the equation used by *Wei et al.* [2001] to calculate the wall loss of particle precursors, we use the same equation to estimate τ_w,

$$\tau_w = \frac{d^2}{4ShD_i} \tag{2}$$

where d is the diameter of tailpipe or transfer line, Sh is the Sherwood Number, and D_i is the diffusion coefficient of ions.

[8] The exhaust flow in the tailpipe is turbulent. Based on the equations given by *Wells and Chamberlain* [1967], we obtain the following equation to estimate τ_w for a turbulent flow,

$$\tau_w = \frac{5.2d^{11/4}}{\dot{V}^{3/4}(\rho/\eta)^{5/12}D_i^{2/3}} \tag{3}$$

where $\dot{V}$ is the exhaust flow rate. ρ and η are the density and viscosity of the exhaust, respectively.

[9] Equation (1) can be solved analytically to give [*ion*] at different exhaust ages (t),

$$[ion] = \frac{[ion]_0}{[ion]_0\beta_r\tau(e^{t/\tau} - 1) + e^{t/\tau}} \tag{4}$$

where $[ion]_0$ is the initial ion concentration.

4. Key Parameters Controlling CI Concentration

4.1. Transfer Time

[10] The transfer time of exhaust from engine exit to the point of dilution t_0 can be estimated as, $t_0 = V/\dot{V}$, where V is the volume of transfer line or tailpipe and $\dot{V}$ is the exhaust flow rate. $\dot{V}$ inside tailpipe depends on the fuel consumption rate and air fuel ratio.

4.2. Ion-ion Recombination Coefficient (K_r)

[11] According to the review article by *Fialkov* [1997], for the hydrocarbon flame close to stoichiometry, the reasonable value of K_r is $2.4 \pm 0.4 \times 10^{-7}$cm^3/s. However, K_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]. It is likely that average mass of ions is larger in fuel-rich flame as more non-volatile and semi-volatile materials are produced. As the mass of ions increases, the ion trapping distance decreases dramatically and hence K_r drops significantly [e.g., *Brueckner*, 1964]. Based on the nature of the motor engine fuel (typically with various additives) and burning conditions (sooting), CIs inside tailpipe are likely to have collected some molecules. The mass distributions of CIs in the exhaust shall depend on the engine types, fuel types and additives, and engine operation conditions. We estimate K_r to be $\sim 10^{-7}$ cm^3/s for 100 amu ions. K_r can drop down to 10^{-8} cm^3/s as the mass of ions increases to 1000 amu.

Table 1. Values of K_s for Ions of Different Mass and the Corresponding τ_s for Diesel and Gasoline Engines

M_i (amu)	K_s (cm^3/s) (assuming d_s = 60 nm)	τ_s (s)	
		diesel engines ($N_s = 10^7$/cm^3)	gasoline engines ($N_s = 10^4$/cm^3)
100	1.4×10^{-6}	0.07	70
400	7×10^{-7}	0.14	140
1000	4.4×10^{-7}	0.23	230

4.3. Time Constant of Ions Due to Soot Scavenging (τ_s)

[12] τ_s is inversely proportion to the number concentration of soot particles (N_s) and the average collection rate of ions by soot particles (K_s). N_s is typically $\sim 10^7$/cm^3 for diesel engines [*Wei et al.*, 2001] and $\sim 10^4$/cm^3 for gasoline engines [*Ristovski et al.*, 1998]. Since the mean diameter of soot particles (d_s) is $\sim$60 nm [*Wei et al.*, 2001] and the size of ions $\ll d_s$, K_s can be calculated as,

$$K_s = \frac{1}{4}\pi d_s^2 v_i \beta = d_s^2\left(\frac{\pi R\overline{T}_{exhaust}}{2M_i}\right)^{1/2}\beta \tag{5}$$

where v_i and M_i are the mean kinetic velocity and mass of ions, respectively. $\overline{T}_{exhaust}$ is the mean temperature of exhaust, and R is gas constant. β is the charge enhance factor and can be estimated based on formulas presented in *Hoppel and Frick* [1986]. It is clear that K_s depends on the mean size of soot particles as well as the size (or mass) of ions. Table 1 shows the values of K_s for ions of different mass and the corresponding τ_s for diesel and gasoline engines. A mean soot diameter of 60 nm is assumed, and the soot charge fractions and enhancement factors reported in *Hoppel and Frick* [1986] are used. We can see that the loss of ions to soot particles inside tailpipe is likely to be significant for diesel engines but negligible for gasoline engines.

4.4. Time Constant of Ions Due to Wall Loss (τ_w)

[13] Equations 2 and 3 show that τ_w is affected by the mass of ions as $D_i \propto M_i^{-2/3}$ for molecular size ions. Diffusion coefficients for ions of 100, 400, 1000 amu (T = 600 K) are estimated as 0.19, 0.08, 0.04 cm^2/s, which lead to corresponding τ_w of 0.09, 0.21, and 0.42 s for a transfer line with d = $\sim$0.5 cm [*Wei et al.*, 2001], and corresponding τ_w of 0.5, 0.9, 1.4 s for typical gasoline vehicles with d = 6 cm (assuming a fuel consumption rate of 2.5 gallons/hour and an air fuel ratio of 14.7).

[14] There is another type of wall loss – the loss of ions to exhaust aftertreatment systems (such as catalytic converter, particulate filter/trap, etc). While the exhaust only experiences very short period of time through the aftertreatment system, the loss may be significant because the diameter of the catalytic converter honeycomb and the particulate filter cross-section are very small.

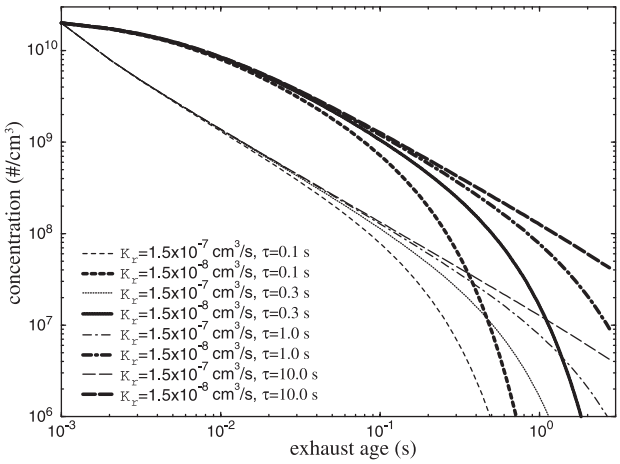

Figure 1. Predicted evolution of total ion concentration (= 2x [ion]) as the exhaust ages inside the tailpipe or transfer line at two different recombination coefficients and four loss time constants.

[15] Below, we study the evolution of ions under a wide range of parameters and compare the results with related measurements.

5. Analytical Results and Comparison with Related Observations of Nuclei Mode Particles

5.1. Analytical Results

[16] CIs in the engine exhaust are likely to have different masses. The values of K_r and τ are different for CIs of different masses. Figure 1 shows evolution of total ion concentrations (= 2 × [ion]) as the exhaust ages inside the tailpipe or transfer line at two different recombination coefficients and four loss time constants. As mentioned earlier, positive ion concentrations of up to 10^{10}–10^{11}/cm^3 have been reported in hydrocarbon flames [*Fialkov*, 1997]. We assume that the initial ion concentration in the combustion zone (t = ∼1 ms) is 10^{10}/cm^3 (i.e., $[ion]_0 = 10^{10}$/cm^3). A larger $[ion]_0$ will give similar $[ion]$ at t = ∼10 ms due to faster ion-ion recombination rate ($\propto[ion]^2$). Figure 1 indicates that the ion concentration at the end of expansion stroke (∼10 ms exhaust age) is around 10^9/cm^3 (with K_r = 1.5 × 10^{-7}cm^3/s as ions are likely to be small during the first 10 ms because of the high temperature). Both K_r and τ affect the ion concentration significantly. Wall loss and soot scavenging become particular important when $t > \tau$.

5.2. Effect of Transfer Line

[17] *Wei et al.* [2001] studied the influence of transfer line residence time (TLRT) on the formation of nuclei mode particles. Different TLRTs were obtained by varying exhaust flow rate in the transfer line. The measured particle size distributions in the diluted exhaust show a clearly bimodal structure. *Wei et al.* [2001] found that the total number of particles in the nuclei mode decreases while their mean diameter increases with increasing TLRT. *Wei et al.* [2001] attributed this to the loss of particle precursors in the transfer line. Since the precursor loss would reduce not only the total number of particles formed but would also lead to less particle growth and smaller particles in the nuclei mode, *Wei et al.* [2001] concluded that the only way to explain this is that some particle nucleation was taking place in the transfer line. This explanation is not convincing because temperature of the exhaust inside the transfer line should be too high (>200°C) for any nucleation of nuclei mode particles. On the other hand, a significant loss of precursor gases in the transfer line is expected to reduce the total volume of particles. However, *Wei et al.* [2001] found that the total volume of particles slightly increases as TLRT increases. This argues against a significant loss of precursor gases in the transfer line. Here we suggest that observed lower number concentration but larger size of nuclei mode particles associated with longer TLRT might be explained more consistently by the loss of ions.

[18] Figure 2 is the same as Figure 1 except it is now in a linear-linear scale and we also include the observed number concentrations of nuclei mode particles measured by *Wei et al.* [2001]. As the exhaust inside the transfer line ages, the ion concentration decreases significantly due to ion-ion recombination and loss to wall/soot. Since all the ions survived the loss in the transfer line are likely to be activated to form nuclei mode particles when the hot rare (i.e., undiluted) exhaust is diluted, the observed reduction in nuclei mode particle concentration with increasing residence time could be explained by the loss of ions in the transfer line. A recombination coefficient of ∼1.5 × 10^{-7}cm^3/s and loss constant time of ∼0.2 s are needed to explain the data points at t = 0.096, 0.126, 0.184 s. These parameters are within the ranges of values we discussed earlier. As t increases, there is a tendency that data points shift to analytical lines with smaller K_r and larger τ. This is expected since those CIs with smaller mass (and hence larger K_r and smaller τ) tend to disappear earlier, leaving behind larger CIs with smaller K_r and larger τ. The observation at t = 2.1 s may be associated with nucleation on ions of largest mass which have smallest K_r and largest τ, or condensation on very small solid nuclei generated during combustion when soot particles form.

[19] Observed lower number concentration but larger size of nuclei mode particles associated with longer TLRT could

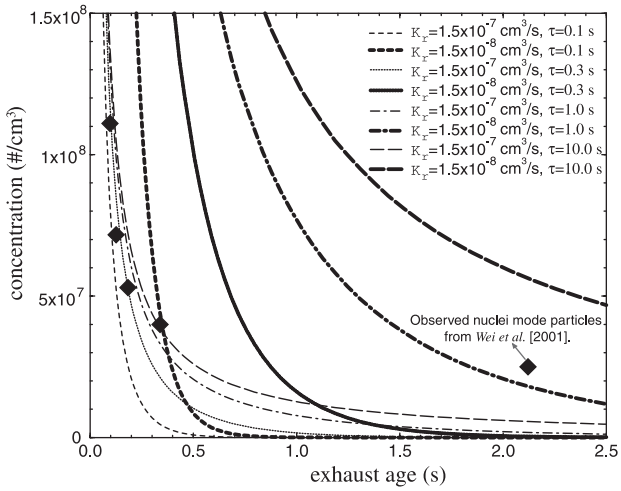

Figure 2. Same as Figure 1 except it is now in a linear-linear scale and the observed number concentrations of nuclei mode particles measured by *Wei et al.* [2001] are included.

be readily explained by the loss of ions in the transfer line. The loss of ions should be more efficient than the loss of precursors as precursors might be re-evaporated from the surface (wall or soot) due to the high temperature (>200°C). Since fewer ions are available for nucleation at longer TLRT, these ions grow to larger size under similar (or slightly less) amount of precursors.

5.3. Effect of Particulate Filter (or soot concentration)

[20] It has been observed that a reduction in soot concentration as a result of cleaner modern engines or of using a particulate filter actually leads to an increase in the nuclei mode particle emissions. Our calculation shows that at $t = 0.5$ s, a reduction of soot concentration from $10^7/cm^3$ to $10^6/cm^3$ increases the ion concentration by a factor of 100 and 9 for 100 amu ions and 400 amu ions, respectively. Since ion abundance after dilution is the limiting factor for the number of NPs formed [*Yu*, 2001], more NP emission associated with reduced soot concentration in diesel exhaust could be explained consistently by the weakened soot scavenging of ions.

5.4. Effect of Vehicular Speed

[21] Measurements of particle size distributions on-road under varied traffic conditions indicate that the number concentration of nuclei mode particles increases while their size decreases with increasing traffic speed [e.g., *Kittelson et al.*, 2001]. On the other hand the volume concentration (dominated by accumulation mode particles) decreases with increasing traffic speed. It is difficult to explain this enhanced formation of nuclei mode particles by assuming that the precursor gas concentrations in the diluting exhaust plume are somewhat higher at higher speeds, as it can't explain why both the size of nuclei mode particles and volume of accumulation mode particles decrease. Here we suggest a possible explanation.

[22] At higher speed, the fuel consumption rate (kg/s) is higher (more power is needed), which leads to higher exhaust flow rate and hence shorter exhaust residence time inside the tailpipe. As we can see from Figures 1 and 2, shorter tailpipe residence time reduces the loss of ions inside the tailpipe and hence increases the concentration of ions available for nucleation when the exhaust is diluted in the atmosphere. Since more ions and hence nucleated NPs compete for similar amount of precursors at higher vehicular speed, the mean size of the nuclei mode particles is smaller which is consistent with the observations. In other words, the different degree of ion loss inside tailpipe due to different tailpipe residence times associated with different vehicular speeds may consistently explain the observed connection between NP emissions and vehicular speeds. We want to emphasize that the effect of vehicular speed on particle size distributions may be complex as the engine operation conditions vary with vehicular speeds. More quantitative study is obviously needed.

6. Summary and Discussion

[23] Due to their potential health effects, volatile nanoparticles emitted by diesel and gasoline engines have received increasing attention. Recently, *Yu* [2001] proposed that the chemiions generated during combustion play a key role in the formation of these nanoparticles. In this paper, the evolution of engine-generated chemiions inside a tailpipe or transfer line is studied and the key parameters controlling chemiion concentration at exit are investigated. The observed impacts of transfer line residence time, soot concentration, and vehicular speed on engine nanoparticle emissions are analyzed.

[24] We find that observed higher number concentration but smaller size of nuclei mode particles associated with shorter transfer line residence time, enhanced nanoparticle emission associated with reduced soot emission, and increase in the number concentration but decrease in size of nuclei mode particles with increasing traffic speed, can all be consistently explained by the reduced loss of ions in the transfer line or tailpipe. The existing explanations of these phenomena focusing on the loss of precursor gases are not able to consistently account for the main observed properties.

[25] The chemiion theory has been shown to reproduce the observed total nanoparticle concentrations, and their sensitivity to fuel sulfur contents and second stage dilution conditions in our earlier study [*Yu*, 2001]. The success of the chemiion theory in explaining the observed dependence of nuclei mode particles on transfer line residence time, soot concentration, and vehicular speed, as discussed in this paper, provides further evidence that the chemiions generated during combustion play a key role in the formation of these nuclei mode particles. Of course, experimental studies following the approaches outlined by *Yu* [2001] are still needed to verify the theory.

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F. Yu, Atmospheric Sciences Research Center, State University of New York at Albany, 251 Fuller Road, Albany, New York 12203, USA. (yfq@asrc.cestm.albany.edu)