Particle nucleation by recondensation in combustion exhausts

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Abstract. Observational and experimental evidence is presented here to verify a hypothesized "recondensation-induced" nucleation mechanism. While analyzing the diurnal variations in particle number concentration in an urban area, intense particle production was found to occur during the commuting hours even when there was no significant photochemical activity. Combustion-induced nucleation processes occurring in fresh automobile exhausts are believed to be responsible for the observed phenomenon. It is hypothesized that, besides the more familiar fuel-sulfur conversion mechanism, particle nucleation may also result from the recondensation of chemicals vaporized from preexisting particles in the intake air during combustion. An experimental verification was performed by heating the ambient air without the use of fuel, then cooling it down to allow for nucleation. A net particle production of over $700,000 \text{ cm}^{-3}$ was achieved during this heating-then-cooling procedure. The results indicate that the recondensation-induced mechanism is potentially important in various types of combustion exhausts.

1. Introduction

At this time of escalating anthropogenic emissions, the effects of aerosol particles have raised great interest in many scientific fields. Because of the different aerodynamic, thermodynamic, radiative, and chemical behaviors associated with their physical dimensions, each scientific field tends to focus on particles of certain size ranges. The ultrafine particles (with diameter less than about 100 nm) in particular have very complex generation and evolution mechanisms, and exhibit diverse effects that have attracted interest in fields including material synthesis, microcontamination, biotechnology, atmospheric radiation, emission control, and public health.

In spite of their great significance, our knowledge of the ultrafine aerosol particles remains rather incomplete. One of the difficulties in understanding the behavior of ultrafine particles stems from the fact that their generation mechanisms vary greatly with different source types and atmospheric conditions. The formation of ultrafine particles in the troposphere and stratosphere normally requires the coexistence of two or more condensable vapors so that homogeneous-heteromolecular nucleation may occur at vapor partial pressures well below those required for monomolecular-homogeneous nucleation. Being the most abundant condensable species in either the natural atmosphere or combustion exhausts, water vapor is no doubt the primary participant in such a nucleation process. The secondary condensable vapors (hereafter, SCV) may include sulfuric acid, nitric acid, ammonia, or organic gases. Among these SCV, sulfuric acid is probably the most prevalent under natural conditions or through anthropogenic emissions. However, there is an ongoing debate on how sulfuric acid vapor is sufficiently produced, especially in near-source situations.

It is commonly believed that photochemical reactions are essential in producing the SCV, as supported by many measurements showing clear diurnal variations in particle mass or number concentrations (e.g., Baltensperger et al., 1997; Raes et al., 1997). This photochemically-induced mechanism has been suggested to operate in various locations far from the emission sources (cf. Covert et al., 1992; Marti et al., 1997; Raes et al., 1997). However, it is questionable whether this mechanism may be applicable to near-source situations such as industrial, automobile and aircraft exhaust plumes. The observed diurnal variations in remote areas suggest that the daytime build up of aerosol particles occurs in a time scale of several hours. Yet, as demonstrated by many aircraft exhaust studies, one can find ultrafine particles in rather high number concentrations in very early exhaust plumes (e.g., Petzold et al., 1997). Estimations based on classical binary nucleation theory have indicated that a fuel-sulfur to sulfuric acid conversion ratio of a few percent in fresh exhaust might be needed to account for the observed number concentration (Fahey et al., 1995; Kärcher and Farhey, 1997). Yet, calculations based on combustion kinetics have failed to produce such high conversion ratios (Kärcher, 1995; Kärcher and Farhey, 1997; Andronache and Chameides, 1997). As indicated by Frenzel and Arnold (1994) as well as Yu and Turco (1997), such a discrepancy might be explained by the ion electrostatic effects that may enhance particle nucleation.

The aforementioned particle generation mechanisms in fresh aircraft plumes are also likely to operate in other types of combustion exhausts. However, past studies on particle generation from industrial and transportation activities have focused mainly on the photochemically-induced nucleation mechanism (e.g., Liebsch and de Pena, 1982; Kerminen and Wexler, 1995). Less attention was given to particle generation from combustion-derived SCV as reported by the aircraft plume studies. This study not only suggests such a combustion-induced (as opposed to the photochemically-induced) mechanism may operate in industrial and automobile combustion exhausts, but also proposes that the SCV do not have to be derived from the fuel itself. As is discussed in detail below, the SCV may be derived from the vaporization of preexisting particles contained in the intake air during combustion.

2. Observation

Because the number and mass concentrations of aerosol particles are poorly correlated variables (Tuch et al., 1997), it is difficult to gain direct evidence of particle nucleation from mass-based measurements such as PM_{10} (mass concentration of particulate matter smaller than 10 μm in aerodynamic diameter). Nevertheless, one can still gain some insight from those measurements by looking at signatures that contradict the photochemically-induced mechanism. For instance, Chow and Watson (1995) found that the diurnal variations in aerosol mass loading in urban areas exhibit two distinct peaks that are strongly associated with morning and evening commuting activities. Such a bimodal pattern is quite different from the unimodal afternoon peak found in many remote areas. In urban areas, particle generation (at least in terms of mass) from automobiles may overwhelm that from the photochemical mechanisms.

Mass measurements do not directly provide information on newly formed ultrafine particles because they normally contribute very little to the total mass. Therefore the increase in aerosol mass loading during traffic hours as shown by Chow and Watson (1995) may very well be a result of the emission of soot particles, unburnt fuel and ashes, as well as particle resuspension from the road surface. To distinguish ultrafine particles from these relatively large particles, one needs to further look into particle number concentration measurements, especially for those in the ultrafine particle size range.

Figure 1 shows the particle number concentration (N) and PM_{10} (M) taken in an urban area (Taipei, Taiwan) over a two-month period (mid-September to mid-November) in 1997. Particle number concentration is measured with a Scanning Mobility Particle Sizer (TSI model SMPS-3934C), which classifies particles in the diameter range of 10 ~ 520 nm into 109 channels. The PM_{10} data are averages of measurements taken with an hourly beta attenuation monitor at three nearby ambient air sampling sites. Note that the diurnal pattern of M averaged over these two months is very similar to the annual average. By comparing the diurnal variations of N and M , one may notice several distinct features: 1) both N and M exhibit two major peaks; 2) the morning and evening peaks of M lag behind those of N by 3 ~ 4 hours and 1 ~ 2 hours, respectively; and 3) the build up of N starts about 1.5 hours before sunrise (which occurs between 5:40 and 6:10 a.m. for the corresponding period of time). While the N peaks can be directly linked to the climax of traffic activities, the M peaks are apparently controlled by additional factors as indicated by the time lag. For example, the continuous build up of M after morning traffic hours may be attributed to photochemical reactions that gradually convert gas-phase pollutants (such as SO_2 and NO_x) into condensing acid vapors. This mechanism operates longer for the morning peak, thus causing higher M and a longer time lag in the morning than in the evening. However, the same mechanism does not necessarily apply to the situation between 4 and 7 a.m., not only because of the limited photochemical activity but also because of the opposite trends in N and M during this period of time.

The sharp increase of N before dawn took place everyday during the two-month period regardless of the weather patterns. This result strongly suggests that photochemical activities do not dominate particle generation in the urban atmosphere. The most probable cause of such an intense particle generation is the early-morning traffic. However, if this is indeed the case, then the question why M does not increase in accordance with the increase of N remains to be answered. If the particle nucleation is promoted by the fast conversion of fuel-sulfur into sulfuric acid vapor in fresh exhaust, a process proposed by many aircraft

Figure 1: Diurnal variation of fine-particle number concentration (N) and PM_{10} (M) measured in the City of Taipei during the Fall of 1997.

Figure 2: Schematic diagram of the recondensation-induced nucleation process. Gaseous chemicals may vaporize from preexisting aerosol particles during combustion heating, then condense (nucleate) into many ultrafine particles during cooling.

exhaust studies, it then necessarily leads to an increase in total aerosol mass. Yet, the newly formed ultrafine particles are normally quite low in mass because of their small sizes. So, when the traffic activity is not yet intense, the increase in mass from the newly formed particles might not be strong enough to reverse the nightly decreasing trend of M in spite of their numerous numbers. Note that the total particle volume concentration measurable by the SMPS typically varies by less than $5 \mu m^3 cm^{-3}$ (equivalent to $5 \mu g m^{-3}$ if a density of $1 g cm^{-3}$ is assumed) during the commuting hours. It is also possible that much of the ultrafine particles are semivolatile, and mass losses could occur from particle samples (cf. Leong et al., 1983). Unfortunately, insufficient information is available for further discussions.

Another mechanism that may easily account for the increase in particle number concentration without the addition of total particle mass is shown schematically in Figure 2. Most motor vehicles (especially motorcycles which are one of the major emission contributors in many Asian cities) do not filter out preexisting fine particles in the intake air for combustion. Among the common compositions of aerosol particles, H_2SO_4 and HNO_3 have relatively low boiling point ($444.7^\circ C$ and $83^\circ C$, respectively), whereas NH_4HSO_4 and $(NH_4)_2SO_4$ decompose quite readily at temperatures of a few hundred degree Celsius. During the combustion process, those preexisting particles are very likely to vaporize under engine temperatures that often exceed $1000^\circ C$. Ultrafine particles are particularly vulnerable to vaporization, not only because of their small sizes but also because of their volatile compositions. As a result, the exhaust from motor vehicles is very likely to contain a significant amount of sulfuric acid, as well as many other condensable vapors, regardless of the fuel composition. Fast cooling of the exhaust while mixing with ambient air then triggers intense particle nucleation during the recondensation of these vapors. A further examination into the observational data discussed previously for more information is necessary before introducing an experimental verification of the above hypothesis.

In the exhaust air there may exist two types of particles that are attributes of the ambient air: 1) preexisting particles that are not completely vaporized during combustion, and 2) those entrained into the exhaust due to mixing. Many studies have shown that existing particle surface area tends to retard the nucleation process in an air parcel because of the vapor competition effect (cf. Covert et al., 1992; Weber et al., 1995). Therefore, the production of particles through the "fuel-sulfur conversion" mechanism and the photochemically-induced mechanism tends to be weaker when the ambient aerosol particle

content is higher. The "recondensation-induced" mechanism, on the other hand, tends to be stronger when the ambient aerosol content is higher because it feeds on these preexisting particles. An analysis of the hourly values of N may provide a test for the above argument. Here, let ΔN ($\equiv N_{\max} - N_{\min}$, where $N_{\max}$ is the peak value of N , and $N_{\min}$ is the minimum before the peak) represent the production of new particles during peak traffic hours, and $N_{\min}$ represent the initial ambient particle concentration. A simple statistical analysis of the daily ΔN and $N_{\min}$ then gives a correlation coefficient of 0.63 and 0.70 for the morning and evening traffic hours, respectively. Although only moderately significant, these positive correlations between ΔN and $N_{\min}$ still indicate a more favorable recondensation-induced mechanism than the fuel-sulfur conversion mechanism. However, it was also found that the correlation between ΔN and M averaged between the time of $N_{\min}$ and $N_{\max}$ is insignificant (slightly negative). Such a discrepancy might result from the fact that the larger particles, although the major contributor to M , do not vaporize completely during combustion.

3. Experiment

The combustion-induced nucleation of ultrafine particles in fresh exhaust was measured using a SMPS at a distance of 10 cm behind the tailpipe of a spark-ignition automobile. The average particle number concentration in the exhaust was $12,000 \text{ cm}^{-3}$, about four times that in the ambient air. Note that in this measurement it took about 15 s for the exhaust air to travel through the sampling tube. When the tube length was quadrupled, the number concentrations increased to more than $400,000 \text{ cm}^{-3}$ in spite of a greater chance of loss to the tube walls, indicating the length of time is important to the overall particle production. The above number concentrations are of a similar magnitude as those reported by Petzold et al. (1997) for aircraft exhausts ($> 10^5 \text{ cm}^{-3}$) and those by Kittelson (1998) for spark-ignition automobile exhausts ($10^5 \sim 10^6 \text{ cm}^{-3}$). Although uncertainties exist because of the wall losses, the above results nonetheless indicate that the combustion-induced nucleation mechanism is rather effective.

To further examine the combustion-induced mechanisms, the next experiment was performed with a focus on the process depicted in Figure 2. First, the ambient air was heated indirectly by passing it through a ceramic work tube placed in a hot furnace. In this way, the heating effect was obtained without the influence of fuel sulfur or unburnt fuel. The heated air was then allowed to cool down to room temperature before reaching the SMPS. Particle nucleation occurred primarily during this cooling stage. Note that the combustion temperature in automobile engines is typically between 1000 and 3000°C. With an experimental temperature of 1000°C, the result shown next represents only a minimum effect. Figure 3 shows the particle size distribution in the heated air, as well as that measured immediately before the heating experiment. It is clear that the heated air contains significantly more ultrafine particles and fewer particles in the upper size range than the unheated air. The number concentration increased from $3,100 \text{ cm}^{-3}$ to $710,000 \text{ cm}^{-3}$ during the heating-then-cooling procedure. Few particles were detected when the same procedure was repeated on purified air, indicating the furnace itself is not a significant particle source. Since there were no other foreign sources, the production of the particles shown must have been caused by the recondensation of chemicals vaporized from the preexisting particles during the heating process. Although the water vapor content in the heated air was significantly lower than that in actual combustion exhausts, a great number of particles were produced nonetheless, indicating a very efficient particle production mechanism.

Figure 3: Size distributions of aerosol particles in the heated and unheated air.

The average particle volume concentration measured by the SMPS was $1.75 \mu\text{m}^3 \text{ cm}^{-3}$ in the unheated air and $39.9 \mu\text{m}^3 \text{ cm}^{-3}$ in the heated air. Such a large difference suggests a contribution of chemicals from particles with sizes greater than the upper detection limit of the SMPS. In addition, one may also notice in Figure 3 the existence of particles several hundred nanometers in diameter in the heated air. Because the duration of the heating-then-cooling procedure was too short for the newly formed particles to reach such sizes by either condensation or coagulation, these particles are most likely residues from the preexisting aerosol particles that were not completely vaporized. The incomplete vaporization may be a result of either their large sizes or non-volatile compositions. Additional tests have shown an increase in particle production with higher furnace temperatures, which indicates the degree of vaporization is dependent upon the degree of heating. However, a quantitative relationship between the degrees of vaporization and heating as a function of particle size and composition is yet to be accomplished.

4. Discussion and Conclusion

The observational and experimental results shown in the previous sections suggest that the combustion process is in effect converting a few large aerosol particles into numerous ultrafine particles. Such a resizing process has many adverse influences upon humans and the environment. For instance, at similar mass concentrations, ultrafine particles are more effective in scattering sunlight and thus have a stronger effect on visibility and radiative energy balance in the atmosphere. Also, because of the dependence of deposition efficiencies on sizes, ultrafine particles are adsorbed easier in the respiratory system. Hence, as suggested by many recent studies, ultrafine particles are more hazardous to human health than micron size particles at similar mass concentrations (cf. Kittelson, 1998). These effects may lead to the question if our current emission control strategies are appropriate. Although emission standards for diesel engines have lead to dramatic reductions in particle mass emitted, some low-emission engines actually produce much higher concentrations of ultrafine particles (Kittelson, 1998). Also, past efforts on emission control have focused on cleaner fuels, exhaust traps and catalysts. Based on the experiments shown above, one may also consider reducing the emission of ultrafine particles by filtering out the preexisting particles from the intake air.

Removing the preexisting aerosol particles of course does not warrant a complete reduction in ultrafine particles in combustion exhausts, because particles may still be produced by the fuel-sulfur conversion mechanism or from the unburnt fuel. The aircraft studies seem to suggest that there are much more sulfate

particles than the soot particles in the exhausts especially under high fuel-sulfur conditions (cf. Zhao and Turco, 1995; Brown et al., 1996). Yet, so far in this study the relative importance between the recondensation-induced and fuel-sulfur conversion mechanisms has not been made clear. In the following, an attempt was made to evaluate these two combustion-induced mechanisms by estimating the amount of SCV each may have. For the recondensation-induced mechanism, the amount of available SCV is of the same order as the ambient aerosol mass loading. Due to a lack of information on automobile exhausts, however, the available SCV for the fuel-sulfur conversion mechanism is inferred from a few aircraft exhaust studies.

By assuming a fuel-sulfur content of 0.5 g kg^{-1} , Brown et al. (1996) calculated the maximum mole fraction of total sulfuric acid (TSA, in both the gaseous and particulate forms) to be 4.5 and 14 ppbv in plumes from supersonic high-speed civil transport and Boeing 707 aircraft. Direct in-flight measurements by Curtius et al. (1998), on the other hand, showed somewhat lower values. They found TSA up to 1.3 ppbv in a sulfur-rich situation (fuel-sulfur content of 2.7 g kg^{-1}), and TSA not much greater than the local background level of $0.015 \sim 0.050$ ppbv in a sulfur-poor situation (fuel-sulfur content of 0.022 g kg^{-1}). In comparison, the amount of SCV available from ambient aerosol mass loading is typically about a few tens of ppbv in the urban atmosphere, and could reach 1 ppbv in the free troposphere (cf. Jaenicke, 1993). Thus, in terms of the amount of available SCV, the recondensation-induced mechanism is more effective in producing ultrafine particles than the fuel-sulfur conversion mechanism, especially when a low-sulfur fuel is used.

The simple estimation presented above suggests that the recondensation-induced mechanism is potentially important in the production of new particles in the combustion exhausts of not only automobiles but also high-flying aircraft under certain conditions. Besides having an abundant source of SCV, the recondensation-induced mechanism has two other advantages over the fuel-sulfur conversion mechanism: 1) the vaporization process reduces the surface area of preexisting particles, thus minimizing their competition for the SCV; and 2) in addition to the sulfuric acid, ammonia, hydrochloric acid and other common compositions in the preexisting particles may all vaporize and participate in a multi-molecular homogeneous nucleation process, which is much stronger than one with only sulfuric acid and water vapor (cf. Coffman and Hegg, 1995; Weber et al., 1996).

This study provided only a very preliminary analysis of the recondensation-induced mechanism. Future investigations could include the measurements of particle production rate as a function of temperature and ambient aerosol mass loading, and the degrees of particle vaporization as a function of their size and chemical compositions, as well as analysis of the chemical composition of the re-condensed aerosol particles.

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