

Evolution of particle number distribution near roadways— Part I: analysis of aerosol dynamics and its implications for engine emission measurement

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Abstract

Studies have suggested that aerosol number concentrations may be better correlated to health effects than mass concentrations so that the high particle number concentrations in the vicinity of freeways raise concerns regarding adverse health effects on people living there. Thus, it is important to understand how particles transport and transform near roadways for regulatory purposes. Driven by different mixing forces, exhaust dilution near roadways usually experiences two distinct dilution stages after being emitted—‘tailpipe-to-road’ and ‘road-to-ambient’. The first stage dilution is induced by traffic-generated turbulence and the dilution ratio usually reaches up to about 1000:1 in around 1–3 s; the second stage dilution is mainly dependent on atmospheric turbulence, the additional dilution ratio is usually about 10:1, and the process usually lasts around 3–10 min. The aerosol dynamical processes, such as nucleation, condensation and coagulation were qualitatively investigated in the first stage. For the second stage, condensation and dilution were the major mechanisms in altering aerosol size distribution, while coagulation and deposition play minor roles. Based on the analysis, a modeling structure for a mechanistic roadway air quality model is proposed. Our study also indicates that in order to simulate the first stage, ‘in-tailpipe’ measurement of aerosol size distribution and condensable material concentrations in their original phase states is necessary. The implications for dilution tunnel design are discussed.

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1. Introduction

Epidemiological studies have implied the association between small particles and adverse human health

effects, such as lung cancer (Pope et al., 2002) and heart attacks (Brook et al., 2002). Aerosol number distributions have been widely measured for urban, rural and remote environments and various sources to characterize properties of small particles, especially those in the ultrafine size range (<100 nm). Our study has been focusing on numerical modeling of the number distributions of urban and regional aerosols, providing a tool for ultrafine particle control strategies (Zhang and

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Wexler, 2002a). Like most of other air quality models, it aims to establish ‘source–receptor’ relationships. Atmospheric processing connects source to receptor, which can be further divided into plume processing and ambient processing (Fig. 1). Ambient and plume processing are different in both of their temporal and spatial scales: ambient processing usually takes hours or days in large geographical domains, such a $5 \times 5 \text{ km}^2$ cell for a typical urban domain or $30 \times 30 \text{ km}^2$ cell for a typical regional domain; in contrast, plume processing takes place within a few hundred meters from sources and source profiles can be changed dramatically in just few minutes. We have analyzed the relative importance of different atmospheric aerosol processes in ambient processing (Zhang and Wexler, 2002a). However, given that the current ambient air quality standards are mass-based, an accurate, number-based and size-resolved particle emission inventory, which is essential for a number-based model, will not become feasible in the near future. Thus, developing a rational way to estimate particle number emissions from plume processing of sources such as power plant plume and roadways is necessary.

Over the years, substantial efforts have been made to understand the chemical and physical processes inside plumes from point sources, theoretically and numerically (Seigneur et al., 1983; Kerminen and Wexler, 1995; Kumar and Russell, 1996). In spite of extensive laboratory studies on engine emissions (Hildemann et al., 1991; Abdul-Khalek et al., 1999; Schauer et al., 1999b; Maricq et al., 2002b), there are few investigations of how mobile emissions evolve and affect urban and regional air quality, establishing a link between sources and receptors. On the other hand, several field studies found that particle number concentrations in the vicinity of freeways were significantly higher than their background level (Zhu et al., 2002a, b) and evidence suggests that fresh traffic exhaust is hazardous, independent of background concentrations (van Vliet et al., 1997; Brunekreef et al., 1997). Therefore, it is important to understand how particles transport and transform near roadways especially regarding the public health of those traveling on and living in close proximity to freeways. In this work, we shall investigate the evolution of aerosol number distributions near roadways and elucidate the

aerosol dynamics near mobile sources. The ultimate goal, while beyond this work, is to develop a mechanistic air quality model able to simulate the ‘tailpipe-to-ambient’ process and serve as a ‘plume-in-grid’ model for mobile sources, which will greatly improve our understanding of the effects of mobile emissions on ambient air quality and human exposure.

The conditions near mobile emission sources differ from typical background conditions in that (1) particle number concentrations are much higher, and (2) dilution processes are much faster and stronger, which not only reduces number concentration rather rapidly but at the same time may trigger other physical processes like nucleation. In the current paper, we start by analyzing the dilution processes and elucidating the characteristics of different dilution stages. Then the interactions between dilution and other aerosol processes, namely condensation and evaporation, coagulation, nucleation and deposition, are described. Based on the results from our analysis as well as from measurement studies conducted by various researchers, we propose a two-stage modeling structure, namely, ‘tailpipe-to-road’ and ‘road-to-ambient’, of a mechanistic roadway air quality model. Finally, we discuss experimental work that is needed to build such models, such as ‘in-tailpipe’ measurement, and the implications of our study on real-world dilution tunnel design. Part II of this series (Zhang et al., 2004) presents the analysis and simulation results of the ‘road-to-ambient’ process near two major freeways in Southern California.

2. Near-roadway dilution is a two-stage process

Various field measurements have been conducted to measure the particle number concentrations near roadways and dilution is found to be the dominant mechanism that alters particle number concentrations (Shi et al., 1999; Zhu et al., 2002a, b). Let us assume that when a plume dilutes, every small parcel of air contains a certain fraction f of the original exhaust, and $1-f$ of the ambient. f is called the dilution factor in this study. Dilution ratio, defined as $1/f$, has also been used by others to denote dilution (Kim et al., 2001; Shi et al., 2002). For inert species, the plume concentration, C_i , is given by, $C_i - C_{i,A} = f(C_{i,E} - C_{i,A})$ where, $C_{i,E}$ and $C_{i,A}$ refer to the concentrations in the exhaust and the ambient, respectively (Kerminen and Wexler, 1995). A similar equation governs aerosol number concentration, $n(D_p, t)$, experiencing a dilution process with $n_E(D_p, t)$ and $n_A(D_p, t)$, the number concentrations of exhaust and ambient particles, $n(D_p, t) - n_A(D_p, t) = f((n_E(D_p, t) - n_A(D_p, t)))$. In a similar manner, temperature in the air parcel, T , changes approximately as

$$T - T_A = f(T_E - T_A), \quad (1)$$

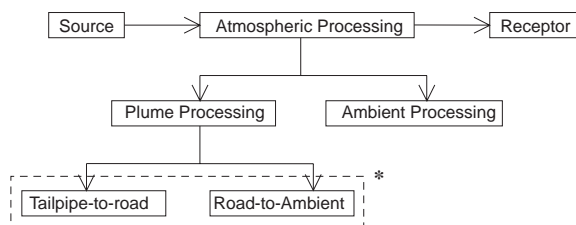


Fig. 1. A source-to-receptor relationship *for mobile sources.

where T_E and T_A are exhaust and ambient temperatures, respectively.

Turbulence dilutes the exhaust. Consider an exhaust parcel emitted from the tailpipe, dispersing to the background. This parcel experiences two very distinct dilution processes. First it is diluted by the strong turbulence generated by moving traffic, moving it from tailpipe to roadside, and then by atmospheric turbulence induced mainly by wind and atmospheric instability, moving it from roadside to the ambient. Hereafter we name the first stage ‘tailpipe-to-road’ and the second stage dilution ‘road-to-ambient’, respectively.

Although dilution is the most important mechanism in altering pollutant concentrations in both stages, the magnitudes are conspicuously different. The relative dilution magnitudes can be quantified by comparing turbulence dissipation rates in the two stages, namely ϵ_{mt} and ϵ_{atm} , respectively. Dissipation is characterized by u^3/l , where u is the characteristic speed and l the characteristic length scale. For turbulence generated by moving traffic, the characteristic speed and the length scale are the speed and the height of moving vehicles, respectively. For atmospheric turbulence, wind speed is the characteristic speed and the integral length scale of atmospheric turbulence close to the ground is about 50–100 m (Baker, 2001). Table 1 lists the values and results of the comparison. That ϵ_{mt} is usually far greater than ϵ_{atm} indicates that the first stage dilution is much stronger than the second one so that the first stage dilution is almost independent of atmospheric conditions, while mainly depending on traffic speed and road conditions. This traffic-generated turbulence dominates dispersion near highways and its importance for initial dispersion of pollutants has been recognized (Rao et al., 2002).

Previous field studies and laboratory experiments have indicated two such distinct dilution stages. Kittelson et al. (1988) noted that the dilution ratios of 1000 or more are reached 1–2 s behind the tailpipe. In their wind tunnel simulation of heavy-duty truck exhaust dispersion, Kim et al. (2001) determined the dilution ratio increased exponentially to a value of 350

within 2.54 m downstream of the exhaust stack outlet, which occurred within 0.5 s. Shi et al. (2002) found the dilution ratio could reach 1000–4000 just 2–3 m away from the passing vehicles (in less than 1 s). While the studies above were generally describing the first-stage dilution, some others, which measured particle concentration away from the roads, focused on the second-stage dilution. In their measurement on fine particle emissions on Minnesota highways using a mobile emissions laboratory, Kittelson et al. (2004) showed that particle concentrations measured 10 m from highway were <3.5 times as much as those 700 m from highway. Shi et al. (1999) measured particle size distributions at three adjacent sites in Birmingham, UK, where particle concentrations 2 m from curbside were only about 4 times higher than those measured 30 and 100 m away. In a similar field campaign conducted in Brisbane, Australia by Morawska et al. (1999), the results demonstrated that particle concentrations 10 m from the road were about twice as high as those 60 m and further away.

All these studies support our proposed two-stage dilution process. In order to compare the dilution with other aerosol processing mechanisms, we need to describe it in a more quantitative way. But the dilution process happens so fast that an analytical expression of dilution time scale would be a very steep function and not practical to use. So, we make the following approximations generalized from the case studies: (1) the first stage dilution is the process where dilution ratio reaches 1000 in 1–5 s and in the second stage the plumes are further diluted by a factor of 10 in 3–10 min; (2) spatially, the first stage dilution probably ends about 10 m from the curbside and the plumes become ambient-like about 300 m from the road, where the second stage dilution ceases to dominate; (3) exhausts emitted from different types of engines maintain their characteristics in the first stage but generally mix with each other in the second stage. Although this approximation will not be exact for specific cases, the errors of those approximations are within the uncertainties in the literatures cited above.

Table 1
Comparison between the ‘tailpipe-to-road’ and ‘road-to-ambient’ processes

	Stage 1 ‘tailpipe-to-road’	Stage 2 ‘road-to-ambient’
Mixing force	Moving traffic	Atmospheric shear and stability
Characteristic speed (m s^{-1})	20–30	1–10
Characteristic length scale (m)	2–3	50–100
Dissipation rate ($\text{m}^2 \text{s}^{-3}$)	2500–14000	0.01–20
Spatial range	Tailpipe to roadside	Roadside to ambient
Dilution ratio	~1000 in 1 s	< 10 in 10 min
Temperature gradient	Steep	Flat

Because of the extremely high dilution ratio, diluted exhaust temperature has already dropped to ambient level at the end of the first stage, which has significant implications in terms of aerosol thermodynamics. Since the bulk-phase volatile compound vapor pressures depend strongly on temperature, they change dramatically in the first stage and virtually remain the same level in the second stage. In the next section, we discuss aerosol dynamics in details.

3. Aerosol dynamics in dilution process

Dilution has been shown to be an important process influencing aerosol concentrations and distributions. Then the question arises whether dilution is so dominant that other aerosol process can be neglected in the model simulation without significant loss in accuracy. For instance, whether particles grow or shrink significantly during the dilution process? We try to examine two major issues here: (1) are new particles formed? (2) will newly formed particles as well as pre-existing particles grow or shrink significantly during the dilution process? These questions can be answered by studying their interactions with dilution. This section is organized in the following way: the aerosol dynamics in gasoline and diesel engine exhausts is investigated separately in tailpipe and the first stage dilution; then the evolution of a characteristic aerosol distribution will be studied for the second-stage dilutions. The chemical species we focus on are sulfate and organic compounds, since they are the likely candidates to trigger nucleation or lead to significant particle growth in such a short time.

3.1. The first-stage dilution in diesel exhausts

The ‘tailpipe-to-road’ process starts when exhaust is just emitted, so the initial conditions are the gas and particle compositions and concentrations at tailpipe exit. But there are few pre-dilution tailpipe, i.e., ‘in-tailpipe’,

aerosol size distribution studies and pre-dilution tailpipe composition measurements are not available yet. Schauer et al. (1999b, 2002) measured gas- and particle-phase emissions rate of organic compounds from late model medium duty diesel trucks, gasoline-powered automobiles and light-duty trucks. The emission rates were given in mass per kilometer driven, from which we were able to obtain the concentrations in the tailpipe by assuming fuel compositions, air/fuel ratios, vehicle fuel consumption rates and exhaust temperature. Table 2 presents the results. However, since this experiment was designed for measuring mass emission at the ambient level (Schauer et al., 1999a), the results did not reflect emissions in their original phase state at tailpipe exit. We will show that particle growth is actually very sensitive to the initial phase states and the importance of ‘in-tailpipe’ measurement will be discussed in a later section. But for now, we use those results as a best estimate for total mass emissions.

Our investigation of aerosol dynamics in the first-stage dilution was carried out under a simplified but illuminating scenario, where dilution, condensation and coagulation were simulated. The basic equations used have been discussed in our previous work (Zhang and Wexler, 2002a) and are not reiterated here. It is assumed that exhausts come out of the tailpipe with a single log-normal aerosol size distribution that we call ‘combustion-induced’; it takes 1–3 s to reach a dilution ratio of 1000; $\text{H}_2\text{SO}_4(\text{g})$ is then compared to its threshold value, C_{crit} , which is the gas-phase concentration of sulfuric acid required for binary nucleation to take place and can be estimated from following formula (Jaeger-Voirol and Mirabel, 1989; Wexler et al., 1994): $C_{\text{crit}} = 0.16 \exp(0.1T - 3.5 \text{rh} - 27.7)$, where C_{crit} is in $\mu\text{g m}^{-3}$, T is in Kelvin, and rh is scaled 0–1. When the critical ratio, $\text{H}_2\text{SO}_4(\text{g})/C_{\text{crit}}$, becomes greater than 1, nucleation occurs instantaneously, giving birth to fresh nuclei in another log-normal distribution, which we call ‘dilution-induced’. Six cases with different parameters were simulated as listed in Table 3. Case 0 is our base

Table 2
Estimation of ‘in-tailpipe’ concentrations based on Schauer et al., 1999b, 2002.

Engine type	Organic emissions			
	Semi-volatile gas-phase		Particle-phase	
	Emission rate (mg km^{-1})	Tailpipe concentration (mg m^{-3})	Emission rate (mg km^{-1})	Tailpipe concentration (mg m^{-3})
Medium-duty diesel	66.1	8.1	43.68	5.36
Light-duty catalyst-equipped gasoline-powered	7.35	1.78	1.45	0.35
Light-duty noncatalyst-equipped gasoline-powered	100.8	20.7	414.89	85.3

Table 3
Parameters in different cases in simulating the first-stage dilution

Case ID	Combustion-induced particles		Time duration (s)	Gas-phase low volatility conc. (mg m^{-3})
	Number conc. ($\# \text{ cm}^{-3}$)	Median diameter (nm)		
0	10^8	50	1	2.7
1	10^8	80	1	2.7
2	10^9	50	1	2.7
3	10^8	50	3	2.7
4	10^8	50	1	1.0
5	10^8	50	1	4.0

case. In Cases 1 and 2, the combustion-induced particles have larger surface areas caused either by larger number or larger mean diameter. The time durations of all cases were assumed to be 1 s except Case 3, where it is 3 s. In Cases 0–4, we split the measured particles concentration evenly back into gas and particle phase at the exit of tailpipe. In Cases 4 and 5, there was a factor of 4 differences in gas-phase concentration to demonstrate their effect on particle growth.

3.1.1. Nucleation

Nucleation results when partial pressure is much greater than vapor pressure for nucleating species. The partial pressure is simply proportional to the dilution factor ($p \propto f$). The vapor pressure, p° , is a function of temperature, which in turn is a function of dilution factor. Close to the tailpipe, the emission temperature far exceeds ambient so the complete relation given in Eq. (1) reduces to ($T \propto f$). Therefore the vapor pressure is related to the dilution factor by $p^\circ \propto \exp(-\Delta H/RfT_E)$, so the saturation ratio is proportional to $f \exp(-\Delta H/RfT_E)$, where ΔH is the latent heat of vaporization of the nucleating species. As f decreases rapidly upon dilution immediately after emission, this function becomes very large so the supersaturation ratio may become high enough to induce nucleation. At the same time due to their low volatility and the existence of large surface areas of particles in the plume, sulfuric acid and many organic compounds condense quickly on the particles, which may or may not suppress the nucleation. Since nucleation favors compounds with both low volatility and low-molar volume in the condensed phase (Zhang and Wexler, 2002b), high-carbon number organics, which usually possess very low vapor pressure but have significantly larger condense-phased molar volume, are less likely to be the nucleating species than sulfuric acid, which may take a binary form (with water) or ternary form (with water and ammonia). Fig. 2 displayed the viability of sulfuric acid-induced nucleation and the coupling effect of condensation and nucleation. As surface area of combustion-induced particles increases, the critical ratio drops and in extreme cases like Case 2,

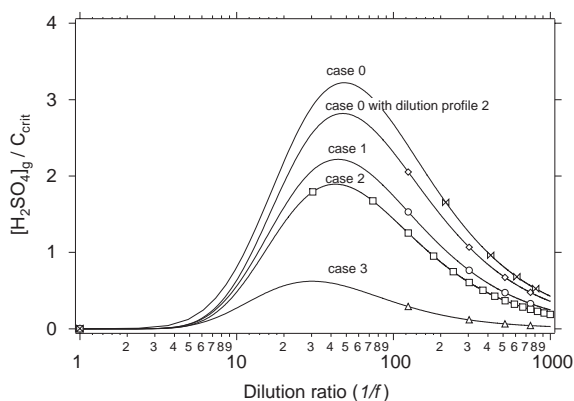


Fig. 2. Viability of sulfuric-acid initiated nucleation.

the nucleation could be totally quenched. The possibility for nucleation could also become lower if the time duration is longer (Case 3), which demonstrates that extremely rapid dilution is crucial for obtaining supersaturation where nucleation is possible, which may have important implication in designing dilution tunnels or interpreting experimental results.

3.1.2. Coagulation

First we evaluated coagulation caused by turbulent shear, which has a timescale of $\tau_{ts} = \rho_p / (48\hat{m}_p \sqrt{\varepsilon_k / 120\nu})$ (Wexler et al., 1994), based on the coagulation coefficient due to turbulent shear $K_{12}^{TS} = (\pi\varepsilon_k / 120\nu)^{1/2} (D_{pl} + D_{ps})^3$ (Saffman and Turner, 1956), which was shown to be applicable under typical urban atmospheric conditions (Zhang and Wexler, 2002b). From a dissipation rate ε_k of 2500–14000 (Table 1), τ_{ts} is about 10^{18} s, because these tiny particles have such small cross-sectional area that shear is insufficient to bring them together.

Fig. 3 demonstrates the effect of Brownian coagulation, which was generally minor so a linear scale was used to evince the differences. The increased surface area generally amplified its effect in reducing nucleation mode particle concentration (Case 1), but very large

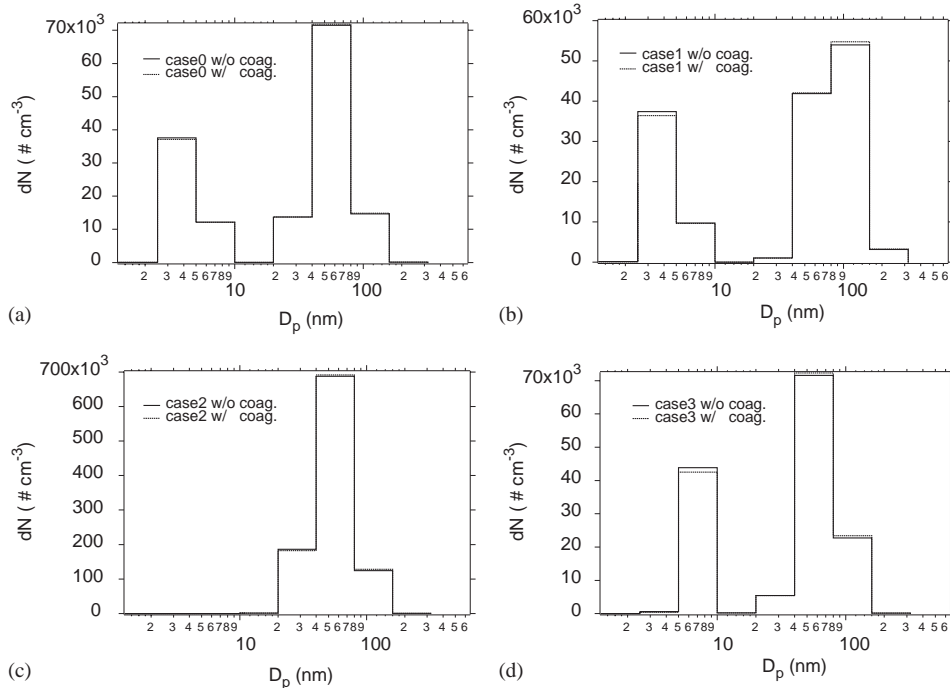


Fig. 3. The effect of Brownian coagulation on aerosol number distribution in first stage dilution for (a) Case 0, (b) Case 1, (c) Case 2 and (d) Case 3.

surface areas would suppress nucleation as discussed earlier, so there were no nucleation mode particles in the first place (Case 2).

3.1.3. Condensation

As discussed earlier, decreases of temperature lead to exponential decreases in vapor pressures. As a result, the highly super-saturated vapors could make the timescale of condensation as short as 0.1–1 s. Thus, even if the time duration is only several times longer than the timescale for condensation, aerosol size distribution will change dramatically due to growth. This effect can be clearly seen in Case 3 (Fig. 3c), where it takes 3 s to reach 1000 dilution ratio instead of 1 s for Case 0. So employing longer residence time in emission measurements may significantly change the original partition of condensable compound between gas and particle phase, which in turn strongly affects the aerosol growth behavior as illustrated by the comparison of Cases 4 and 5 (Fig. 4a and c). This synergetic effect explains why measurements designed for characterizing mass emissions may not be appropriate for characterizing number emissions.

3.1.4. Dilution profile

In the simulation, we adopted the dilution profile measured by Kim et al. (2001) with its original form

$D(x) = 17.6 x^{1.3}$ (Donghee Kim, pers. comm.). Another dilution profile, $D(x) = 7.01x^{0.955}$, measured by Kittelson et al. (1988) and denoted as dilution profile 2 in Fig. 2, was also simulated, predicting higher maximum critical ratio for nucleation. The comparison indicates that the dilution profile, mainly dependent on vehicle types and traffic conditions (Chang et al., 2003), may also affect the occurrence of nucleation. Thus it is worth further measurements, simulations and turbulence mixing studies are needed to elucidate this process.

To conclude this section, new particle formation is very likely in the first-stage dilution of diesel exhaust and occurs when the dilution ratio is around 30–80 (Fig. 2); the growth of nucleation mode particles could be significant and is very sensitive to the amount of condensable materials remaining in the gas phase at tailpipe exit; coagulation is usually too slow to significantly change aerosol size distributions in this stage.

3.2. The first-stage dilution in gasoline engine exhausts

There have been several studies on gasoline engine exhausts conducted by various researchers and no convincing evidences of nucleation have been found yet (Maricq et al., 2002a; Zhang and Wexler, 2002b). This sharp contrast between gasoline and diesel engine

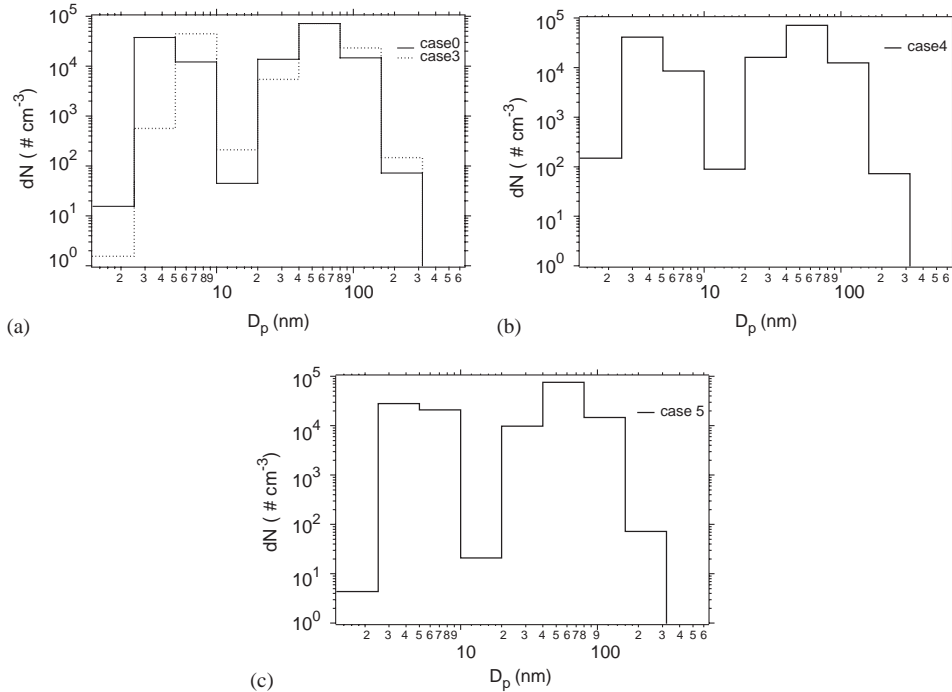


Fig. 4. The growth of nucleation mode particles for (a) Case 3, (b) Case 4 and (c) Case 5.

exhausts questions whether there are nucleation events in gasoline exhaust at all. Our calculations showed that in terms of sulfuric acid concentrations, gasoline engine exhausts still favor nucleation. So very likely nucleation is occurring, but probably the fresh nuclei cannot grow to the detectable size under experimental or real-world conditions. Zhang and Wexler (2002b) proposed the hypothesis that these fresh nuclei have been fully neutralized by ammonia produced by the catalyst system so that the acid-catalyzed chemical reactions, which are crucial to the early growth of these nuclei, are precluded. Then those small nuclei are easily subject to scavenging by larger particles. So unlike diesel exhaust, the characteristic particle size distributions measured in gasoline exhaust were usually mono-modal with a possible ‘hidden mode’ below the particle size detection limit. Given the fact that gasoline engine powered vehicles usually account for over 70% of the traffic fleet on freeways, further efforts should be made to characterize exhaust from this type of engine.

3.3. The aerosol processes on the second-stage dilution

In the second stage dilution, exhausts from different types of engines mix with each other. The aerosol size distribution has multiple modes and number concentrations are around 10^5 cm^{-3} close to freeways, where the

Table 4

Modal fitting of a typical number distribution measured near Highway 405, Los Angeles, CA

	Mode I	Mode II	Mode III	Mode IV
N ($\# \text{ cm}^{-3}$)	50,407	11,419	20,980	19,963
D_{pg} (nm)	12.50	22.65	32.87	62.30
Ln (std)	0.44	0.21	0.28	0.58

‘road-to-ambient’ process spatially starts and it takes about 5–10 min until the exhaust is diluted to ambient. Here, we perform timescale analyses for a typical number distribution measured near Highway 405, Los Angeles, CA (Zhu et al., 2002a). Detailed simulations will be presented in Part II of this series (Zhang et al., 2004). The measured size range was 6–220 nm. Fitting the distribution with log-normal modes, as shown in Table 4, enabled us to extend the size range from 1 nm to 1 μm . Fig. 5 shows the condensational growth timescale τ_G and coagulation timescale τ_{coag} (Zhang and Wexler, 2002a).

3.3.1. Coagulation

For most particle sizes, τ_{coag} was much larger than the duration of the second-stage dilution. Note that τ_{coag} shown in Fig. 5 was estimated based on

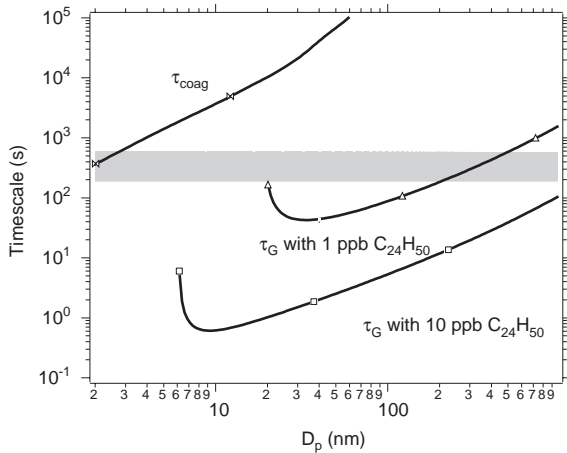


Fig. 5. Condensational growth timescale τ_G and coagulation timescale τ_{coag} in stage 2. The gray swath denotes the dilution timescale (3–10 min).

initial concentrations, and would increase by another magnitude due to dilution in this stage. Clearly, coagulation does not play an important role in the second-stage dilution for particles larger than 10 nm. However, coagulation will have some effect on particles below 10 nm or under slow dilution conditions.

Recently, Jacobson and Seinfeld (2004) simulated the three-dimensional evolution of gas and particle emissions in the vicinity of a freeway, accounting for dilution, coagulation of emitted particles, and condensation of gases. They concluded that coagulation, even possibly enhanced by van der Waals forces and fractal geometry of particles, did not reproduce the rapidity of evolution of the particle size distributions observed by Zhu et al. (2002a,b).

Considering τ_{coag} is about one to two magnitudes slower than the dilution scale (~ 3 min), coagulation can be neglected for the distributions and dilution conditions in the Highway 405 and 710 studies. Most likely, this conclusion applies to most heavily trafficked corridors.

3.3.2. Condensation/evaporation

Lack of composition measurement posed an obstacle to evaluate the effect of condensation/evaporation on particle size distribution, so we had to assume a lumped, average composition for the condensable material in the gas phase. However, only ppb levels of $\text{C}_{24}\text{H}_{50}$ (for instance) could lead to substantial growth of particles smaller than 100 nm as demonstrated in Fig. 5 by τ_G values similar to or much smaller than the second stage dilution timescale. Our detailed analysis in Part II of this work supports the contention that condensation/evaporation persist throughout the second stage.

4. Structure of a ‘plum-in-grid’ for mobile sources and its implications to engine emission measurements

Based on above analysis of aerosol dynamics near roadways, we propose a mechanistic roadway air quality model to simulate plume processing and serve as a ‘plume-in-grid’ model for mobile sources, whose structure is illustrated in Fig. 6. Meteorological data is fed into Model I, the ‘tailpipe-to-road’ model, which contains three main parts: the transportation module processes traffic fleet composition and speed; a turbulence mixing module predicts spatial and temporal mixing ratios after applying tailpipe emission profiles to traffic fleet; and a chemical physical module, which is incorporated into the turbulence module, simulates particle dynamics, including nucleation and condensation/evaporation. Model I produces gas composition and concentration as well as aerosol distribution and composition, which are inputs for Model II, a mechanistic module simulating condensation and evaporation incorporated into an atmospheric dispersion model. The outputs of Model II, the size and composition specified particle emission rates, are sent to the host model as emission input.

There have been great experimental efforts toward building such a model, such as studies of ‘real-world’ dilution rates (Kim et al., 2001; Kittelson et al., 2004) and effect of vehicle mixing on dilution ratios (Chang et al., 2003). Nevertheless, much work still needs to be done. From a mechanistic point of view, the mobile sources are composed of individual tailpipes. We have demonstrated in Section 3.1 that an accurate assessment of ‘in-tailpipe’ emission, that is, measuring gas and particle-phase exhaust pollutants in their original phase states, is crucial for evolution of aerosol number distribution. Without such initial conditions, i.e., initially hot concentrations of nucleating and condensable materials, mechanistic simulations of nucleation and condensation will not be possible. Furthermore, since pollutants from different sources may be different in their toxic properties and may correspond to different control strategies, it is very important to distinguish the particles produced in the combustion process from those by dilution-induced nucleation, which also requires knowledge of ‘in-tailpipe’ emission. Moreover, separating emissions from dilution details provides a platform for engine characterization inter-comparison.

As we discussed earlier, the condensation of highly super-saturated vapor is very sensitive to the time duration of first stage dilution. However, since hot exhaust is difficult to measure directly, using traditional room temperature dilution techniques will require rapid dilution and rapid measurement in order to retain the original phase states, which in turn requires rapid instrument response time. Recently, hot gas dilution techniques have been proposed by various researchers to

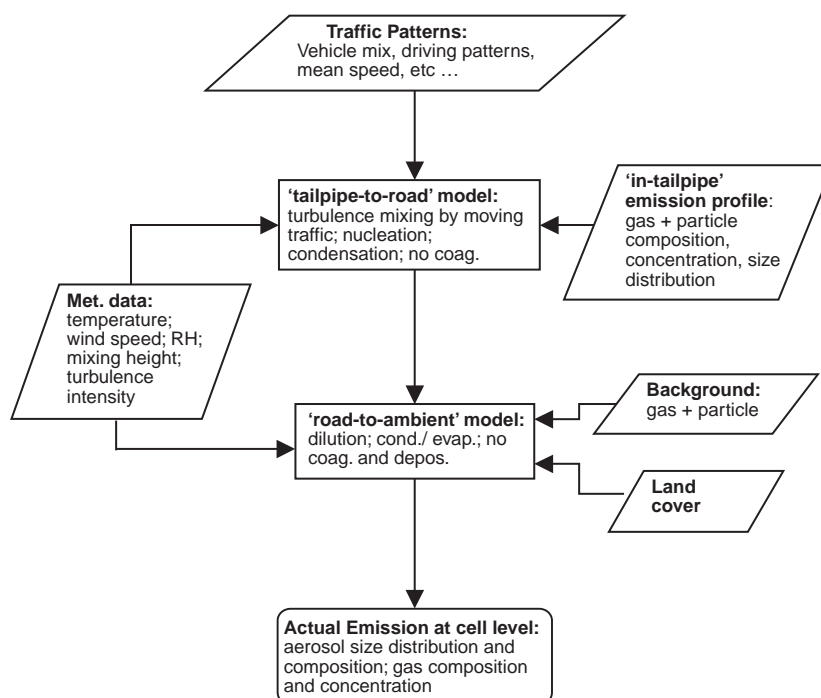


Fig. 6. The modeling structure of a mechanistic roadway air quality model.

conduct such 'in-tailpipe' measurement (Maricq et al., 2002b; Wong et al., 2003). The engine exhaust is first diluted by a similar high-temperature gas. Then, the mixed gas is further diluted to reach the working temperature of the instruments. The advantage of this method is that concentration (thus partial pressure) and temperature (thus vapor pressure) changes are separated, so the time required for dilution and measurement can be longer. However, this technique still needs further improvement and extensive validation to provide a reliable 'in-tailpipe' measurement.

5. Conclusion

Exhaust undergoes two distinct dilution stages after being emitted: The first stage dilution, or 'tailpipe-to-road', is induced by traffic-generated turbulence, often independent of atmospheric conditions, and the dilution ratio usually reaches up to about 1000:1 in around 1–3 s; the second stage dilution, or 'road-to-ambient' is mainly dependent on atmospheric turbulence and the additional dilution ratio is usually within 10:1 occurring in about 3–10 min.

The aerosol dynamical processes, besides dilution, were investigated in the two stages. Exhausts emitted from different types of engines keep their own characteristics in the first stage but generally mix with each

other in the second stage. In the first stage dilution, sulfuric acid-induced nucleation is the dominant particle production mechanism, followed by the condensation of organic compounds, resulting in the rapid growth of nuclei mode particles and relatively slow growth of accumulation mode particles. Although its time span is very short, the first stage is crucial for activation of nuclei mode particles due to high concentrations of condensable species during this period. During second stage dilution, particles can still grow by condensation but the growth rates keep decreasing away from the roadways. At several hundred meters, the aerosol distributions become background-like as a result of dilution. Usually coagulation is not important for the first and second stage dilution, but could be significant for depletion of nano-sized particles when second-stage dilution is slow. The effects of van der Waals forces, fractal geometry and turbulent shear on coagulation between exhaust particles can be neglected for both stages.

A dilution tunnel able to replicate the 'real-world' conditions needs to capture the interaction between dilution and other aerosol processes. Sulfuric acid-induced nucleation strongly depends on the duration of the first stage dilution, i.e., it must be fast enough to keep sulfuric acid in the gas phase, which otherwise will condense on pre-existing particles rather than initiate nucleation. An implication is that dilution time scale and

dilution ratio are equally important for designing dilution tunnels able to simulate 'real-world' conditions. The first stage and second stage not only differ in dilution ratios, but, most importantly, in dilution time scale.

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