



Atmospheric Processes Influencing Aerosols Generated by Combustion and the Inference of Their Impact on Public Exposure: A Review

Zhi Ning, Constantinos Sioutas*

Department of Civil and Environmental Engineering, University of Southern California, 3620 South Vermont Avenue, Los Angeles, CA 90089, USA

ABSTRACT

Combustion-generated aerosols, especially emissions of heavy and light duty vehicles, are the dominant contributors of ambient particulate matter (PM) in urban environments. This paper reviews the atmospheric processes (such as dilution, nucleation, condensation and coagulation) that dominate the dynamics of combustion aerosols following their emission, with a particular emphasis on PM from mobile sources. Atmospheric dilution affects the dynamic behavior of aerosols by shifting the gas-particle partitioning of the semi-volatile component of these aerosols. Our paper discusses the roles of dilution in changing the physico-chemical properties of the ambient aerosols, such as particle size distribution and number concentration, and the degree to which it affects non-labile and semi-volatile PM components. This information is complemented with a discussion of secondary aerosol formation from atmospheric photochemical reactions that involve precursors emitted from traffic sources. Special focus is devoted to the role of gas-phase vapors formed from the evaporation of the semi-volatile fraction of aerosols during dilution. Adding to the common recognition that volatile organic compounds (VOCs) are the major gaseous precursors, these vapors also actively participate in photochemical reactions and contribute to the formation of secondary aerosols. Following this discussion, we review recent findings that link PM semi-volatile components and their redox activity, and we discuss the influence and importance of PM volatility on particle toxicity. Lastly, this paper discusses possible metrics to regulate PM emissions and establish ambient air quality standards that are pertinent to public health, and suggests future investigations aimed to improve our current understanding of the adverse health effects of population exposure to combustion-generated aerosols.

Keywords: Combustion-generated aerosols; Vehicle emissions; Semi-volatile aerosols; Atmospheric process; Public health.

INTRODUCTION

In the last decades, several epidemiological studies have linked adverse health effects of populations exposed to increased ambient fine ($d_p < 2.5 \mu\text{m}$) and ultrafine ($d_p < 180 \text{ nm}$) particles concentrations (Dockery *et al.*, 1993; Laden *et al.*, 2000; Peters and Pope, 2002; Schulz *et al.*, 2005). Particle size determines its deposition site and fraction in human lungs and its potential translocation to other target organs (Donaldson *et al.*, 2000; Oberdorster, 2003; Kreyling *et al.*, 2006). Particle toxicity studies have also linked individual particle chemical components with different adverse health effect. Organics and transition metal PM components have been identified as capable of inducing proinflammatory effects in the lung due to their ability to produce oxidative stress (Nel *et al.*, 1998;

Saldiva *et al.*, 2002). Polar organic compounds such as quinones can act as catalysts to produce reactive oxygen species (ROS) directly (Monks *et al.*, 1992) whereas polycyclic aromatic hydrocarbons (PAHs) can induce oxidative stress indirectly, through biotransformation to generate redox active quinones (Penning *et al.*, 1999).

Particles in the atmosphere can be divided into two broad categories: primary and secondary particles. Primary particles are directly emitted from combustion sources, such as light-duty and heavy-duty vehicles, wood smoke, off-road vehicles, oil combustion of refineries and marine vessels, and stationary sources, such as power plants. In urban areas, vehicular emissions constitute the majority of the primary particles in the atmosphere. These particles are mostly sub-micrometer agglomerates of solid carbonaceous materials residing mainly in accumulation mode (Morawska *et al.*, 2008). Secondary particles are largely composed of sulfate, nitrate, ammonium and secondary organic aerosols (SOA). The inorganic secondary aerosols are formed in the atmosphere from the oxidation of gas-phase precursors such as sulfur dioxide (SO_2) (Seinfeld and Pandis, 1998), nitric oxide (NO) and

* Corresponding author. Tel.: 1-213-740-6134;
Fax: 1-213-744-1426
E-mail address: sioutas@usc.edu

nitrogen oxides (NO_x) (Pinder *et al.*, 2004). By comparison, SOA formation mechanisms have not been fully understood. Generally, SOA may be formed by the oxidation of high molecular weight volatile organic compounds (VOCs) to produce low-volatility products, which subsequently condense onto the existing aerosols (Seinfeld and Pandis, 1998). Particle phase heterogeneous reactions, including those occurring in clouds and fog, may also contribute the SOA formation in the atmosphere (Jang and Kamens, 2001; Jang *et al.*, 2003). Moreover, the gas-particle partitioning of semi-volatile organic aerosols may produce the gas-phase organic compounds in the atmosphere, which subsequently participate in the SOA formation (Robinson *et al.*, 2007).

Atmospheric dynamic processes change the physical and chemical characteristics of combustion generated aerosols after their emission in the atmosphere. Particles from vehicle emissions often display a bi-modal size distribution with a large number fraction of the particles residing in nucleation mode ($d_p < 30$ nm) (Kittelson, 1998). Ambient measurements showed similar bimodal distributions in the proximity of freeways with diesel traffic (Zhu *et al.*, 2002; Ntziachristos *et al.*, 2007a) or when following a diesel vehicle on the road (Vogt *et al.*, 2003; Ronkko *et al.*, 2006). The profile of ambient particle size distribution tends to change significantly with elevated numbers of nucleation mode particles during photochemical episodes due to the formation of secondary aerosols (Moore *et al.*, 2007). Photochemical reactions in the atmosphere also lead to the alteration of particle chemical composition, thus creating seasonal and diurnal variations in the chemical characteristics of ambient aerosols. This review discusses the major atmospheric processes that dominate the dynamics of combustion related aerosols and synthesizes the current understanding of particles toxicity in the context of their adverse health effect of public exposure.

ATMOSPHERIC PROCESSES AND COMBUSTION RELATED AEROSOLS

Following almost immediately the emission of PM from primary combustion sources, atmospheric processes dominate the dynamics of their behavior in the atmosphere and influence their characteristics. These processes include direct particle formation involving nucleation of gaseous precursors and/or their condensation onto pre-existing particles, gas-particle partitioning of primary semi-volatile PM with atmospheric dilution, and further secondary particle formation by means of photochemical reactions. The following sections review our current understanding of the major processes that influence combustion aerosol dynamics based on observations and findings reported in the recent literature.

Nucleation and Condensation

Combustion sources, such as vehicle engines, emit a complex mixture of gas vapors and particulate matter (PM). Nucleation and condensation are the dominant processes

controlling the dynamics of the mixture shortly after their emissions from vehicles. During the dilution phase, the hot mixture of vapors and particles of the exhaust is rapidly cooled, resulting in super-saturation of low volatility gaseous compounds in the exhaust and the formation of new particles by nucleation of these vapors and – or their condensation onto pre-existing particles (Seinfeld and Pandis, 1998). Nucleation and condensation are two competing processes. The availability of a pre-existing particle surface area and the dilution rate determine the degree to which each of these processes dominates. Low aerosol concentrations favor new particle formation by nucleation and their growth to larger sizes (Kulmala *et al.*, 2000), while high PM concentrations promote condensation of the vapors onto the pre-existing particles (Kerminen *et al.*, 2001).

For vehicles retrofitted with diesel particulate filters and other after treatment control devices, the emitted primary particles are efficiently removed resulting in an overall reduction of total PM mass emission rates. However, the reduced particle surface area also facilitates the formation of nucleation mode particles from organic vapors under favorable temperature and dilution conditions. In some cases, nuclei mode particles may also originate from the nucleation of sulphate formed over the oxidation catalyst by oxidation of sulphur dioxide. The ability of diesel vehicles retrofitted with control devices to produce nuclei mode particles depends on the characteristics of the abatement devices. Some dynamometer studies have reported enhanced formation of nuclei mode particles, consisting of a mixture of sulfate and organic compounds, in vehicles equipped with control devices (Grose *et al.*, 2006). Some other studies have shown that the control device can reduce the particle numbers to undetectable levels, such as the catalyzed continuously regenerating trap (CCRTTM) (Kittelson *et al.*, 2006). Fig. 1 shows an indicative graph comparing particle mass and number emission factors from older (baseline) diesel vehicles, operating without after treatment devices, and vehicles retrofitted with control devices (Biswas *et al.*, 2008). There is a clear trend of increased particle number emissions with decreasing PM mass in vehicles operating with control devices. Similar results were also reported in several other studies (Vaaraslahti *et al.*, 2004; Kittelson *et al.*, 2006).

In the ambient environment, particles formed from nucleation processes mostly reside in the size range below 30 nm, and they usually dominate the particle number concentrations near freeways (Zhu *et al.*, 2002; Ntziachristos *et al.*, 2007a). Fig. 2 shows typical particle size distributions near a busy freeway with a high fraction of diesel traffic. At the sampling locations close to freeway, small particles dominate in numbers and they gradually grow to larger sizes as they move away from freeway, indicating the effects of coagulation and condensation.

Nucleation processes involve binary (such as sulfuric acid and water) and ternary (such as sulfuric acid, ammonia, and water) formation mechanisms (Kulmala *et al.*, 2000). Organic vapors may also participate in nucleation, but they contribute mostly to the growth of

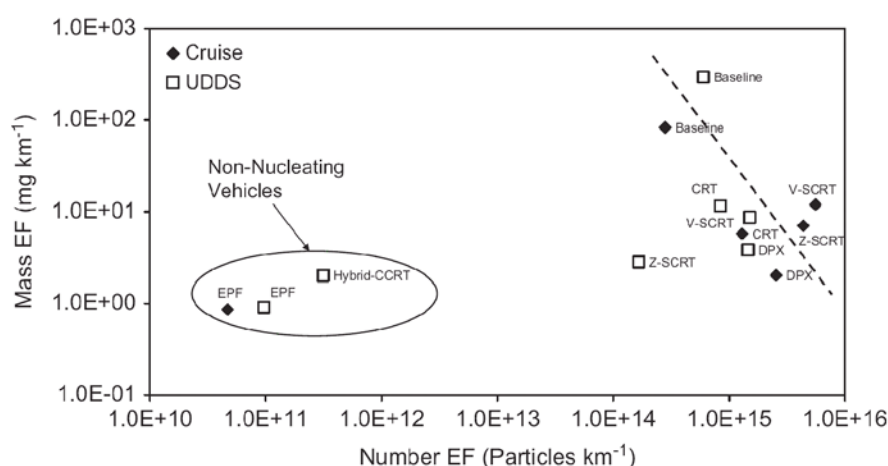


Fig. 1. Number and mass emission factors from different vehicles.

Note: The dots represent the mass and number emission factors from vehicles retrofitted with various control devices. CRT: Continuously Regenerating Technology; SCRT: Selective Catalytic Reduction combined with Continuously Regenerating Technology; V-SCRT: Vanadium based SCRT; Z-SCRT: Zeolite based SCRT; DPX: Diesel Particulate Trap with catalytic wash-coats; EPF: Electric Particle Filter; UDDS: Urban Dynamometer Driving Schedule. Reprinted from Biswas *et al.* (2008) with permission from Elsevier.

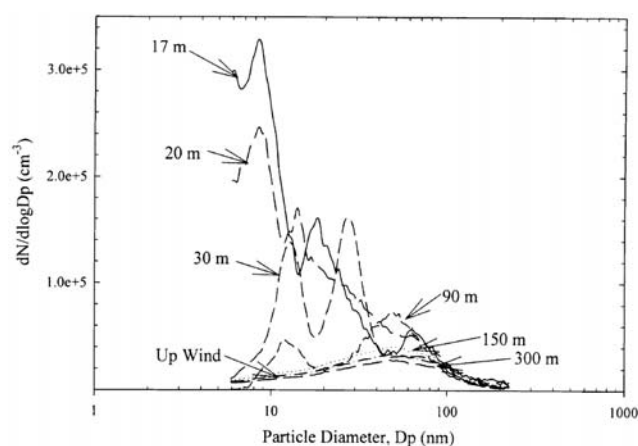


Fig. 2. Particle size distributions at different sampling locations near freeway. Reprinted from Zhu *et al.* (2002) with permission from Elsevier.

freshly formed particles (Kulmala *et al.*, 2004), without being the nucleating agent themselves. In the diesel vehicles exhaust, the ion concentration is too low to account for nucleation mode formation (Ma *et al.*, 2008). However, some studies also proposed that the presence of ions in the atmosphere might affect the nucleation process by stabilizing the nucleating species (Yu and Turco, 2001; Enghoff and Svensmark, 2008). In polluted urban atmospheres, particle formation by nucleation is less favorable than the condensation of vapors of low volatility onto existing particles due to the high particle surface area available for condensation of these vapors (Alam *et al.*, 2003). Charron and Harrison (2003) measured the evolution of particle size distributions near a busy road and showed that semi-volatile vapors from vehicle exhausts favored new particle formation by nucleation and their growth to detectable sizes in the early morning hours, with

low pre-existing particle surface areas of 300 to 500 $\mu\text{m}^2/\text{cm}^3$. However, condensation of condensable vapors onto pre-existing particles dominated during daytime, when the particle surface area increased to 800 to 1100 $\mu\text{m}^2/\text{cm}^3$.

Role of Atmospheric Dilution

Following their emission from mobile sources, particles disperse into the atmospheric background in two distinct dilution stages: 1) tailpipe-to-road dilution by the strong turbulence generated by traffic, lasting about 1–3 seconds, causing dilution up to a factor of 1000, and: 2) atmospheric turbulence-induced dilution caused by the wind and atmospheric instability, which lasts 3–10 min, resulting in an additional dilution ratio of about 10 (Zhang and Wexler, 2004). For non-labile PM species, dilution changes their atmospheric concentrations in the ambient by dispersion. During dilution and cooling, gaseous precursors nucleate or condense onto pre-existing particles. For semi-volatile aerosols, dilution affects their gas-particle phase partitioning and alters the physical (size distribution, concentrations etc) and chemical properties (semi-volatile fraction) of the aerosol.

The dilution ratio (DR) can be calculated based on the ratio of the fleet-average exhaust carbon dioxide (CO_2) concentration over the incremental ambient CO_2 increase, as shown in the following equation (Zhang and Wexler, 2004; Phuleria *et al.*, 2007):

$$DR = \frac{[\text{CO}_2]_{\text{exhaust}} - [\text{CO}_2]_{\text{background}}}{[\text{CO}_2]_{\text{measured}} - [\text{CO}_2]_{\text{background}}} \quad (1)$$

This method has been used to derive the dilution ratio in different environments with significant influence of vehicle emissions, including tunnel environment

(Kirchstetter *et al.*, 1999; Phuleria *et al.*, 2006), on-freeway sites (Kurniawan and Schmidt-Ott, 2006) and ambient sites near freeways (Ntziachristos *et al.*, 2007a).

Dilution Effects on Non-Labile PM Components: For non-labile PM species, such as elemental carbon (EC) or black carbon (BC), organic molecular tracers, heavy molecular weight organic compounds and metals, dilution is the dominant mechanism that determines their ambient concentration levels. For traffic emissions, fuel-based emissions rates are a reliable measure of comparing measurements made at different dilution ratios on a consistent basis. Lipsky and Robinson (2006) measured the fuel-based emission rates of EC from low-load diesel, medium-load diesel vehicles and wood smoke at various dilution ratios. A summary of their results is shown in Fig. 3. EC emission rates from different combustion sources are independent of dilution ratios, appearing as horizontal lines in the figure, which indicates the direct relationship between their ambient concentrations levels and

atmospheric dilution ratios.

Another study by Ntziachristos *et al.* (2007a) compared the ambient BC concentrations measured at locations with different dilution ratios, including the vicinity of freeway, in- freeway measurement with a mobile platform and a tunnel environment. Table 1 summarizes their results. After correcting for dilution, BC concentrations agreed overall quite well among the different environments, especially considering the experimental uncertainties involved in each of these studies. Similar results were also observed for carbon monoxide (CO), which is often used as an indicator of atmospheric dispersion in urban environment.

Dilution effects on semi-volatile PM components: During the first dilution stage, nucleation, condensation and coagulation are mainly responsible for the evolution of overall particle size distribution of emissions in which semi-volatile species play an important role (Zhang and Wexler, 2004).

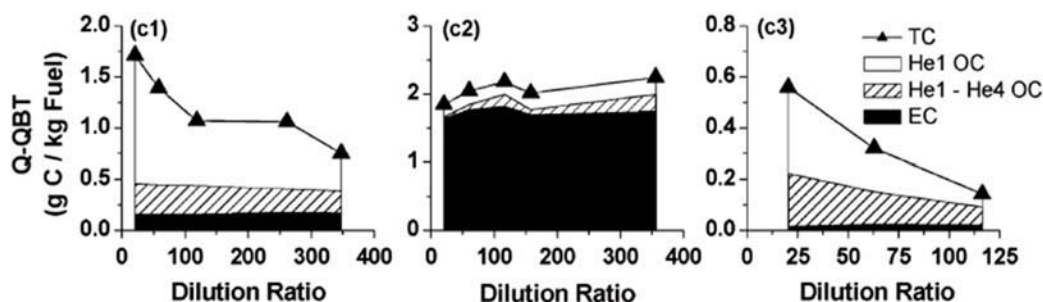


Fig. 3. Fuel-based OC and EC emissions from low-load diesel (left column), medium-load diesel (middle column), and wood smoke (right column) experiments.

Note: He1 OC is the organic carbon (OC) that evolves at 340°C, and He2-He4 OC is the OC that evolves at temperatures greater than 340°C during the OC/EC analysis. Reprinted from Lipsky and Robinson (2006) with permission from ACS.

Table 1. Comparison of concentrations at different environments

	2006 study		Westerdahl <i>et al.</i> (10)		Geller <i>et al.</i> (24)	
location	1–710		1–710		Caldecott Tunnel (Bore 1)	
sampling site	20 m from freeway median strip		mobile lab following traffic		tunnel exit	
period	Feb–Apr 2006		Feb–Apr 2003		Aug 2004	
sampling hours	12 pm–4 pm	5 pm–7 pm			12 pm–6 pm	
passenger cars (1/h)	8359	10250	7580 ^a		4041	
light-duty trucks (1/h)	600	360			91	
heavy-duty trucks (1/h)	1630	1225	1040 ^a		64	
temperature (°C)	21.4	14.4	21		23.3	
RH (%)	42	60			59	
Wind speed (m/s)	2.2	1.2	2.0			
	measured	measured	measured	corrected for DR ^b	measured	corrected for DR ^b
CPC (1/cm ³)	75000	98500	190000	36600 (5400)	637500	92600 (10100)
CO (ppm)	0.27	0.11	1.9	0.28 (0.05)	8.78	2.18 (0.21)
BC (μg/m ³)	4.1	2.8	12	3.4 (0.6)	27.5 ^c	6.8 (1.4)
Relative dilution ratio	1:1			1:10.2 (1.22)		1:7.3 (0.82)

^a Daily averages from CalTrans. ^b Values in parentheses correspond to calculation uncertainty. ^c Elemental carbon. The references listed in the table are as shown in Ntziachristos *et al.* (2007a). Reprinted from Ntziachristos *et al.* (2007a) with permission from Elsevier.

Zhu *et al.* (2002) measured size-segregated particle number concentrations at different distances from several freeways in the Los Angeles basin, as shown in Fig. 4. They observed that the number concentration close to freeway was dominated by very small particles. These particles are semi-volatile in nature and formed by nucleation. Their concentrations decreased dramatically with increasing distance from freeway due to the combined effects of atmospheric dilution, diffusion to available surfaces and evaporation. Coagulation may have also played a minor role in the reduction of particle number concentration and shifted particles distributions towards larger sizes. As argued by Zhang *et al.* (2005), the particle number concentrations even inside the freeway environments are not sufficiently high to lead to coagulation, including agglomeration induced by turbulence. However, limited heterogeneous coagulation of smaller semi volatile nano- particles on larger PM may be possible during the dilution process, as their size decreases and their diffusivity increases progressively when they disperse away from the freeway (Jacobson and Seinfeld, 2004).

Further insights on the evolution of particle number concentrations and size distributions from roadway emission to the ambient were discussed by Zhang *et al.* (2004). Shortly after their emission from the tailpipe, highly concentrated gas vapors experience supersaturation due to their rapid cooling in the atmosphere, which causes them to nucleate and/or condense onto the pre-existing particles, thereby creating a chemically complex aerosol. Following this stage, dispersion from roadway to the ambient occurs, during which the gas-phase concentration decreases, leading to evaporation of some organic compounds in the exhaust whereas other compounds may continue condensing, depending on the relative magnitude of their partial pressure to vapor pressures. The dynamics of volatilization are more pronounced for smaller particles of the UFP range (i.e. < 20 nm), because a higher vapor

pressure is required to keep them from volatilizing compared to larger particles due to the “Kelvin effect”.

By comparing the particle size distributions measured at different distances from freeway, Zhang *et al.* (2004) observed that a large number of particles grow into size larger than 50 nm around 30 to 90 m downwind of the freeways, while some particles shrink to sizes less than 10 nm beyond 90 m away from freeway, and others continue to grow to size larger than 100 nm due to evaporation and condensation, respectively.

Equally informative are the roadway and grid (i.e., urban background) level based emission factors in the study by Zhang *et al.* (2005). The authors of that study computed on-road size-resolved particle number emission factors using concurrently measured carbon monoxide (CO) as a freeway dilution indicator and correlating roadside (i.e., 15 m from the freeway) particle measurements to CO measurements (this is essentially the same methodology illustrated in equation 1, but using CO instead of CO₂ as a tracer of atmospheric dilution). Zhang *et al.* (2005) also extended this analysis to produce unique receptor-dependent, size-resolved, road and grid-level (defined in their case as 150–300 m away from the freeway and considered representative of the urban background) emission factor distributions. Both mileage- and fuel-based particle number emission factors at road and grid levels were determined. Indicative results are shown in Figs. 5a and 5b. The figures show emission factors for particle numbers as a function of particle size obtained at the I-405 freeway during summer (Fig. 5a) and winter (Fig. 5b) periods. In summer time, the emissions of sub-20 nm particles decreased with increasing distance to the freeway, while the emissions of ~50–100 nm particles increased with distance, a counter- intuitive observation that was attributed by the authors to evaporation of sub-20nm and re-condensation on larger PM, due to increased mixing during the summer period. By contrast, in wintertime we see similarities in road-level and grid level emission factors as a function of particle size, with somewhat lower emission factors of very small (i.e. < 20 nm) particles away from roadway, possibly due to some volatilization of these particles despite the relatively lower atmospheric dilution and mixing prevailing during that period. These results are a direct consequence of the aerosol dynamic processes described in the work of Zhang *et al.* (2004).

The evolution of particle size distribution and number concentration is thus accompanied by changes in particle chemical composition, since the partitioning of semi-volatile species may change dramatically with changing dilution ratio to maintain gas-particle phase equilibrium (Hinds, 1982). A large fraction of primary aerosols generated by combustion includes semi-volatile organic components. In the atmosphere, these organic aerosols may undergo gas-particle partitioning depending on their concentrations, meteorological conditions, ambient concentrations of their vapor and PM phases and the degree of dilution (Pankow, 1987). Dilution influences directly the partitioning process by reducing the

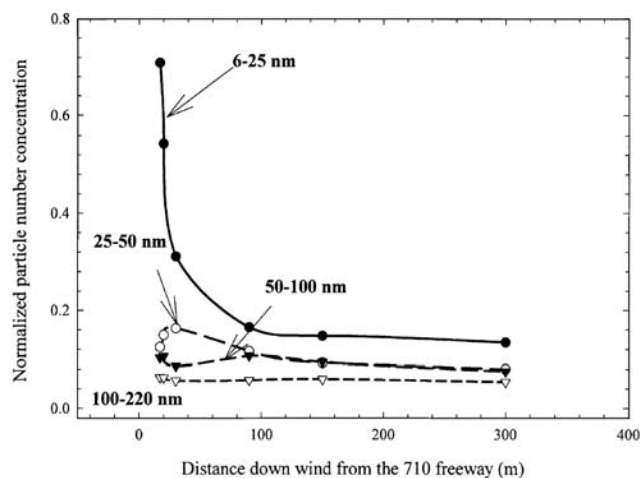


Fig. 4. Normalized particle number concentration from different size ranges as a function of distance from the 710 freeway. Reprinted from Zhu *et al.* (2002) with permission from Elsevier.

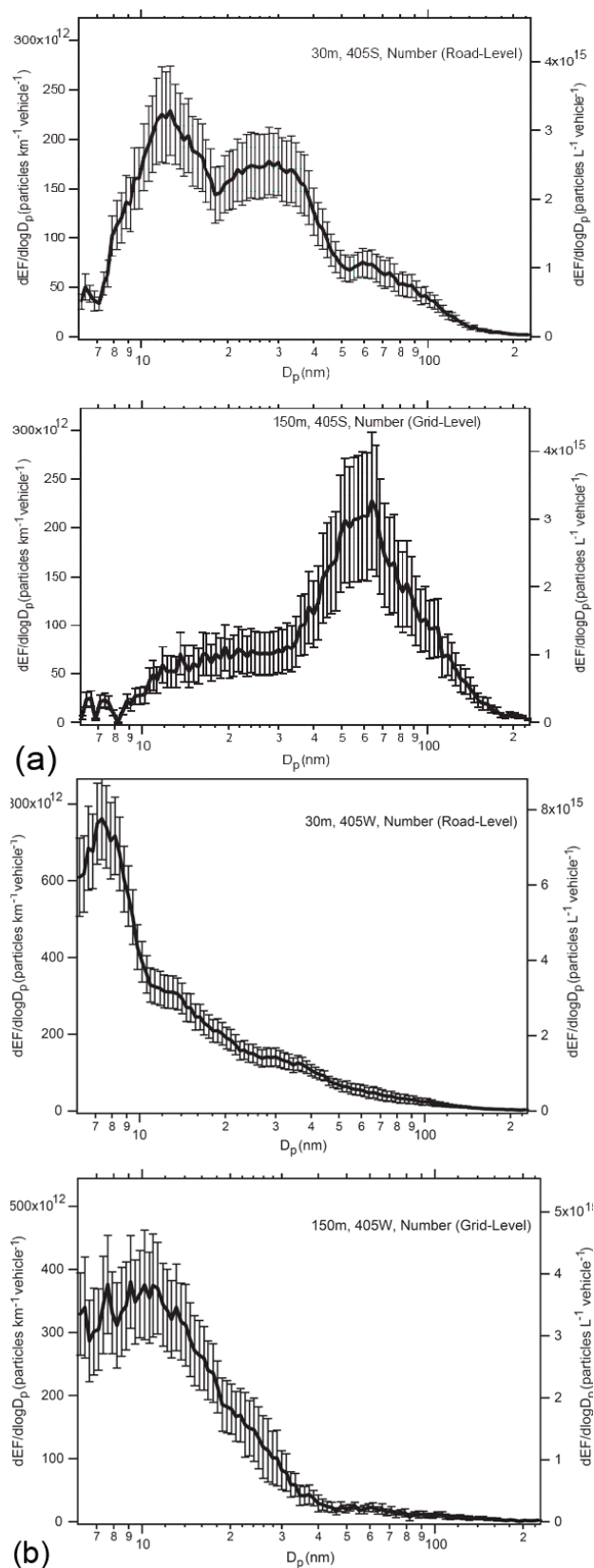


Fig. 5. Distance and fuel-based particle number emission factors in Highway 405 summer (a) and winter (b) studies. The error bars only denote those of distanced-based emission factors. Reprinted from Zhang *et al.* (2005) with permission from Elsevier.

concentrations of both semi-volatile and sorptive species (in the case of adsorption of semi volatile species onto soot particles), which causes semi-volatile species to transfer from particle to gas phases to maintain equilibrium (Lipsky and Robinson, 2006).

Robinson *et al.* (2007) presented a rich set of diesel organic aerosols (OA) partitioning data measured at different levels of dilution, extending from conventional vehicle emission tests to typical atmospheric conditions. Fig. 6 shows that the fuel-based emission factors of organic aerosols decrease with increasing dilution and decreasing concentration, more than what dispersion can explain alone, which indicates substantial evaporation of primary OA with the increasing dilution ratios. From the results reported in that study, only a quarter of the traditionally defined primary OA exists in the particle phase at the levels of ambient dilution conditions with atmospherically relevant concentrations. The measured data showed excellent agreement with the fit curve based on absorptive partitioning (Robinson *et al.*, 2007), along with a 95% confidence interval (CI).

In addition to the factors discussed earlier, the gas-particle partitioning of the complex and dynamic mixture of vehicular exhaust also depends on the volatility of individual organic compounds, which is closely related to their molecular weights and functional groups. Ning *et al.* (2008) compared the fuel-based emission rates of particle phase polycyclic aromatic hydrocarbons (PAHs), hopanes and steranes measured in the near-freeway (black dots), tunnel environment (grey triangles) with different dilution conditions as shown in Fig. 7. These organic compounds have been commonly used as organic tracers for vehicle emissions. By correcting the ratio of the fleet-averaged exhaust CO_2 concentration over the incremental ambient CO_2 increase, the near-freeway sites (Kuhn *et al.*, 2005a; Ntziachristos *et al.*, 2007a) and tunnel site (Phuleria *et al.*, 2006) have an average dilution ratio of about 2500 and 300, respectively.

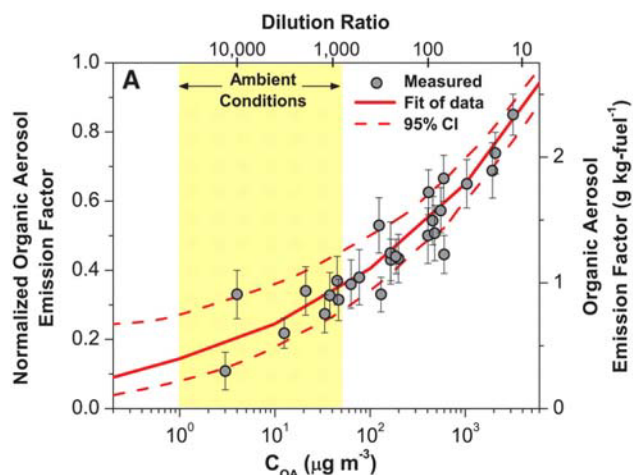


Fig. 6. Fuel-based organic aerosols emission factor as a function of their concentrations and dilution ratios. Reprinted from Robinson *et al.* (2007) with permission from AAAS.

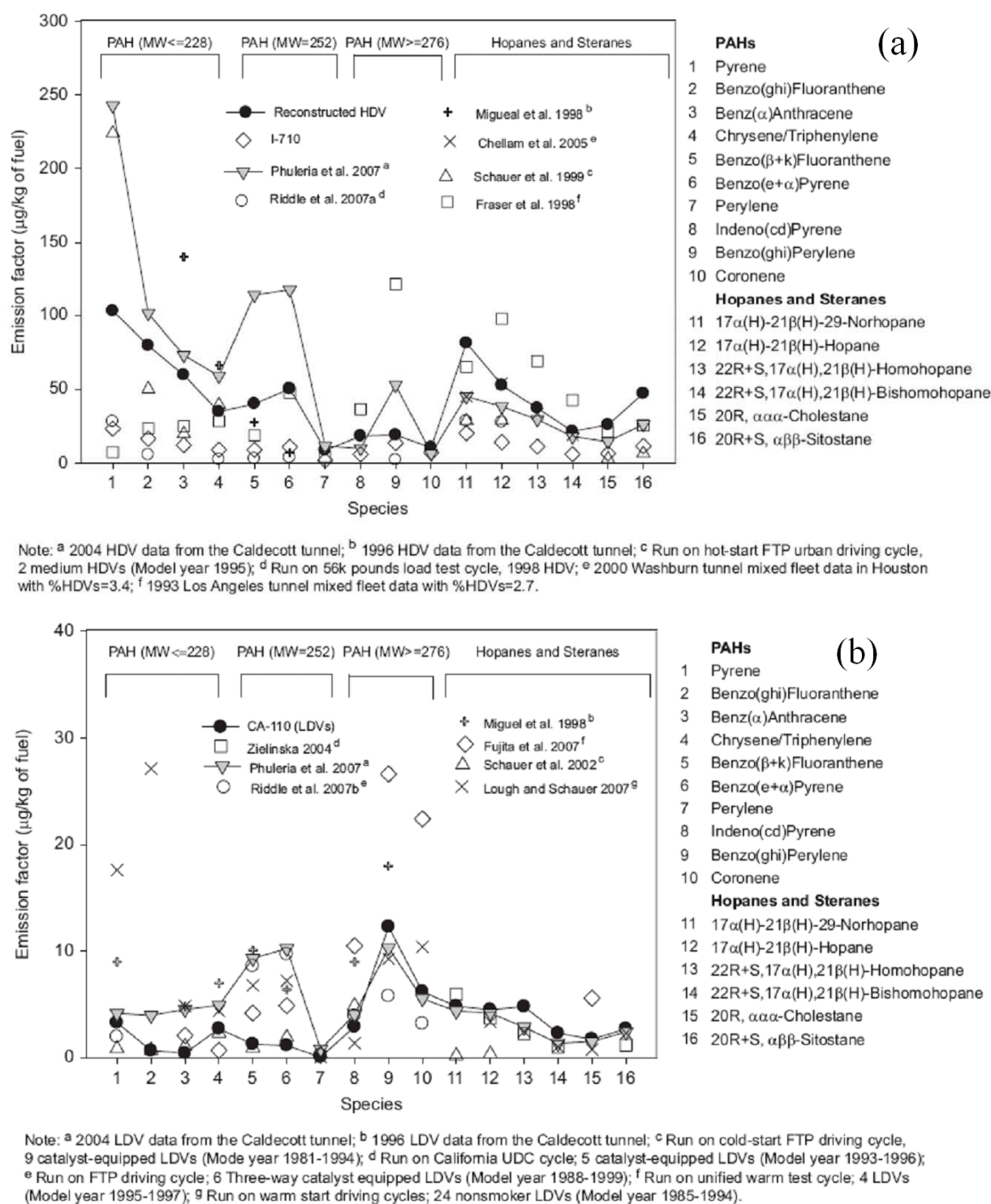


Fig. 7. Fuel-based emission factors of PAHs, hopanes and steranes in various environments with different dilution conditions: (a) I-710 freeway comparison; (b) CA-110 freeway comparison. Reprinted from Ning *et al.* (2008) with permission from Elsevier.

Note: The references listed in the Fig. are as shown in Ning *et al.* (2008)

The estimated emission rates of non-labile species, such as high molecular weight PAHs, hopanes and steranes, were in very good agreement between these environments. However, fuel based emission rates of light molecular weight PAHs measured near freeways only accounted for

about 40–50% of those measured in the tunnel environment, suggesting the likelihood of evaporation of these semi-volatile organic aerosols due to the increasing dilution ratios in the ambient environment compared to the roadway tunnel. This dependence on dilution in the

emission rates of semi volatile species raises significant difficulties in assessing accurately their overall emissions in the context of population exposure, considering that atmospheric mixing and dilution have strong local, seasonal and temporal variations because of their intrinsic dependence on meteorology. This is clearly one of the greatest challenges in the field of characterizing emissions from the exhaust of vehicles.

Photochemical Reactions of Primary Emissions and Secondary Aerosol Formation

Secondary aerosols comprise a large fraction of fine particles in urban areas. The processes that govern the formation of secondary inorganic aerosols, such as sulfate, nitrate and ammonium, have been well understood; however, the sources and formation mechanisms of secondary organic aerosols have not been fully characterized due to the complex nature of organic compounds in the atmosphere.

Generally, SOA are formed by photo oxidation of gas phase volatile organic compounds (VOC) in the atmosphere. VOC are emitted from a variety of natural biogenic and anthropogenic sources, least of which is combustion processes. Approximately 50% of anthropogenic VOC are emitted by combustion related sources (Barthelmie and Pryor, 1997). Generally, VOC that are capable of forming SOA have more than six carbon atoms since the oxidation products of organic compounds with lower carbon numbers are too volatile to condense at ambient temperature conditions (Hung and Wang, 2006). These high molecular weight VOC species react with photochemical oxidants, such as hydroxyl radicals and ozone, and produce low-volatility oxidation products, such as organic acids, nitro-polycyclic aromatic hydrocarbons (nitro-PAH), etc (Seinfeld and Pandis, 1998). The added functional groups result in an increase in the compounds polarity and molecular weight, and thereby decrease their volatility. These compounds have sufficiently low volatilities to condense onto pre-existing particles or to establish equilibrium between the gas and particle phase (Odum *et al.*, 1996). In the absence of nuclei or ions, nucleation also occurs when the oxidation products with exceptionally low vapor pressure accumulate to reach high concentrations.

A recent study by Ning *et al.* (2007) reported ambient organic compounds concentrations of ultrafine particles (defined as sub -180 nm particles in that study) in summer near a busy freeway near downtown Los Angeles, and discussed the formation of secondary organic aerosols by comparing the average organic compounds concentrations during morning rush hours and afternoon photochemically active periods, each representing primary and secondary aerosols, respectively. Fig. 8 shows the average ambient concentrations of PAHs, *n*-alkanes and organic acids measured in the morning and afternoon. As discussed in the previous section, PAHs are semivolatile organic compounds and they exist in both gas and particle phases. The particle phase PAHs concentrations in the atmosphere are affected by the factors such as their source (or emission)

strength, meteorological conditions and gas-particle partitioning (Bidleman *et al.*, 1986). As shown in the figure, morning (6–9 am) PAH concentrations were consistently higher, when the nearby freeway was busy with traffic during morning rush hours, the atmosphere was cooler and the mixing height was low. The decrease of afternoon PAH concentrations reflected the reduction in freeway traffic, increase in mixing height, and possible volatilization due to the increase in temperature. In addition, PAHs can also react with photo oxidants in the atmosphere such as ozone, hydrogen peroxide (Grosjean *et al.*, 1983; Arey *et al.*, 1988) that would also lower their levels in the afternoon. A similar diurnal pattern is also observed for the *n*-alkanes as shown in Fig. 8b. Fig. 8c shows measured organic acids concentrations in the morning and afternoon. In contrast to the diurnal pattern of PAHs and *n*-alkanes, the hexadecanoic (C₁₆) acid and octadecanoic (C₁₈) acid had much higher concentrations in the afternoon despite the increased mixing height, which is a clear indication of the formation of secondary organic aerosols from photochemical oxidation. However, tetradecanoic (C₁₄) acid, also a photo oxidation product, showed slightly lower concentration in the afternoon, which may be explained by its evaporation through gas-particle partitioning process after formation since it has higher volatility than C₁₆ and C₁₈ acids. These ambient observations verify the formation of secondary organic aerosols in the atmosphere even in the quasi-ultrafine PM range (i.e., < 0.2 μ m).

Various air quality and atmospheric chemistry models have attempted to predict the ambient OA concentrations and simulate the formation of SOA from the photo-oxidation of VOCs. However, predicted OA levels from most of these models have shown persistent discrepancies with measured data, generally underestimating SOA formation (Heald *et al.*, 2008; Russell, 2008). Primary organic aerosols are commonly recognized as non-volatile in traditional emission inventories and air quality models. Based on the discussion of our previously sections, supported also by recent laboratory experiments (Lipsky and Robinson, 2006; Robinson *et al.*, 2007) and ambient measurements (Ning *et al.*, 2008), with the increasing of dilution ratios to ambient conditions, some semi-volatile fraction in the primary OA emissions can also participate in the gas-particle partitioning process. As a result, the evaporation of primary OA may substantially contribute to the overall gas-phase organic compounds in the atmosphere in addition to the VOC that are emitted directly from combustion sources (Shrivastava *et al.*, 2006).

Traditional SOA formation mechanism models mostly account for the VOC, such as monoterpenes and light aromatics, as the dominant gas precursors of photochemical reactions in the atmosphere (Koo *et al.*, 2003; Vutukuru *et al.*, 2006). Robinson *et al.* (2007) proposed a modified OA prediction model which accounts for both gas-particle partitioning of semi-volatile OA and the oxidation of all low volatility gas-phase organic vapors to simulate the formation of SOA in the atmosphere. With

the modified SOA formation framework, Robinson *et al.* (2007) compared the fraction of SOA in total OA as predicted by traditional model (Fig. 9a) that treated

primary OA as nonvolatile, and revised model (Fig. 9b) that included the photo-oxidation of gas-phase organics from evaporation of semi-volatile OA. As shown in the

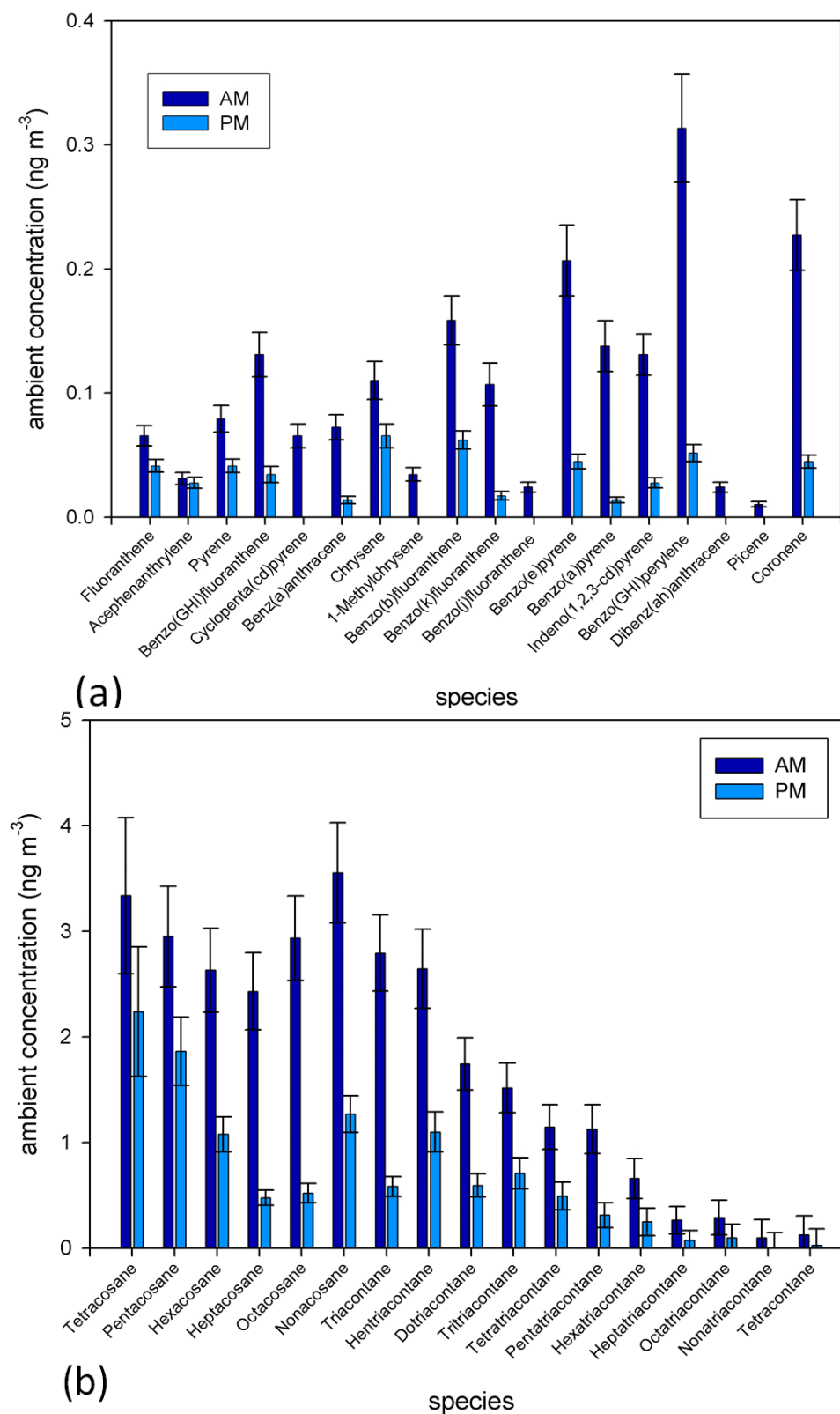


Fig. 8. Average PAHs (a), *n*-alkanes (b), organic acids (b) concentrations of ultrafine particles in the morning (AM) and afternoon (PM). Reprinted from Ning *et al.* (2007) with permission from ACS.

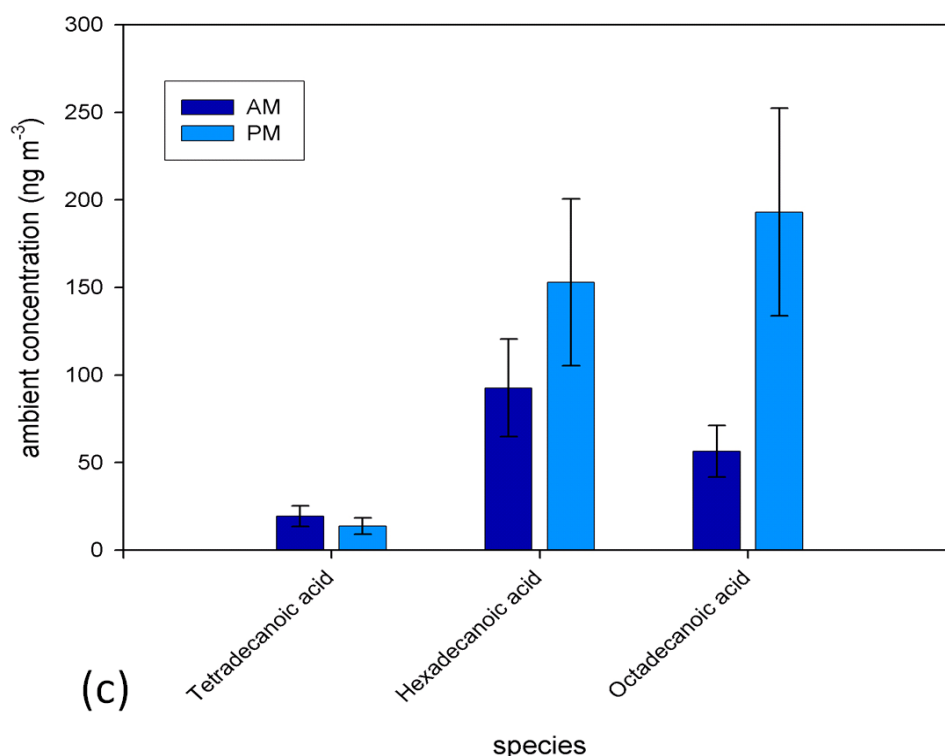


Fig. 8. (continued).

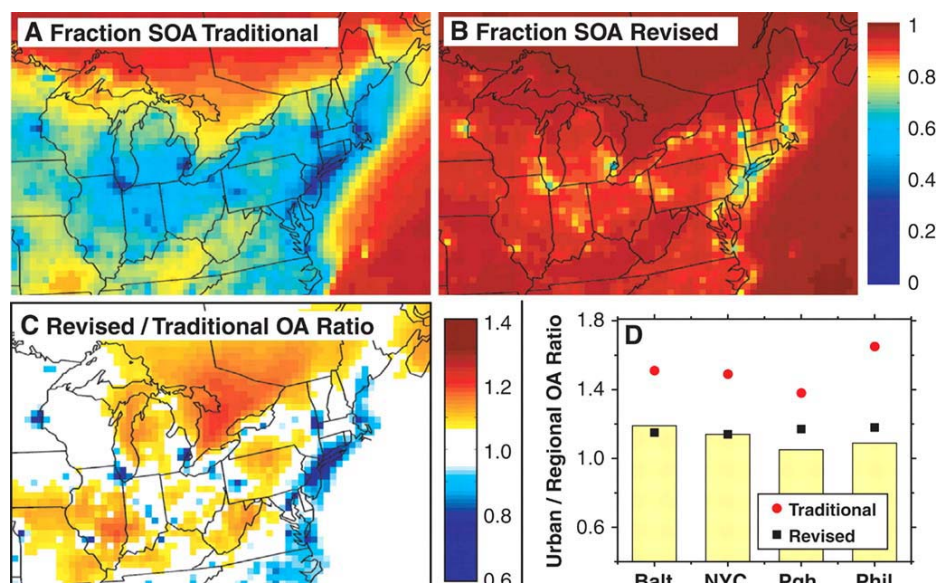


Fig. 9. Predicted SOA fractions in OA from traditional and revised models, and their comparison with ambient measurement data.

Note: Balt, Baltimore, Maryland; NYC, New York City, New York; Pgh, Pittsburgh, Pennsylvania; Phil, Philadelphia, Pennsylvania. Reprinted from Robinson *et al.* (2007) with permission from AAAS.

figures, SOA fraction in the revised model showed substantially higher contribution to OA than in the traditional model, indicating the important role of semi-volatile primary OA in the formation of SOA in the atmosphere. The amendment of traditional model also brought the predicted urban to regional OA ratios to a closer agreement with the ambient measurement data as

shown in Fig. 9d.

PM VOLATILITY AND ITS IMPACT ON PUBLIC EXPOSURE AND HEALTH

In the previous sections we offered extensive discussion of the complex nature of combustion generated aerosols,

which contain both non volatile and semi volatile components (Scheer *et al.*, 2005). The semi-volatile compounds may partition between gas and particle phase in the ambient conditions depending on their vapor pressure and degree of atmospheric dilution (Kuhn *et al.*, 2005b), and participate in photochemical reactions in the atmosphere (Robinson *et al.*, 2007). Consequently, the physical and chemical characteristics of combustion-generated aerosols change dramatically with atmospheric dilution and aging, which may alter their toxic properties and influence their role on population exposures and public health.

Semi-volatile PM contains a wide variety of organic compounds, many of which possess genotoxic and carcinogenic characteristics, such as dioxins, polycyclic aromatic hydrocarbons (PAHs) and their derivatives. Some of these semi-volatile organic species trigger a chain of biochemical reactions in cells, change its redox state and exert oxidative stress. Polar organic compounds, such as quinones, oxygenated PAHs and aldehydes are reported to induce oxidative stress in cells by inducing hemoxygenase-1 expression (Li *et al.*, 2003). A number of bioassays have been formulated to quantify the PM toxicity based on the redox and electrophilic characteristics of PM species, including the dithiothreitol (DTT) consumption rate, ascorbate (reducing agent in lung fluid lining), and the dihydroxybenzylamine (DHBA, transition metal formation) assays (Donaldson *et al.*, 1997; Mudway *et al.*, 2004; Cho *et al.*, 2005). These bioassays estimate the net chemical reactivity of PM without establishing specific mechanistic pathways for PM toxicity. For example, the DTT test measures the ability of particles to catalyze the reduction of oxygen to superoxide and DTT consumption rate gives a fair indication of the formation of reactive oxygen species (Cho *et al.*, 2005).

Previous studies reported strong associations between the PAH content of atmospheric PM samples and DTT (Cho *et al.*, 2005; Ntziachristos *et al.*, 2007b). Biswas *et al.* (2009) measured the chemical composition and redox activity of particles from a variety of diesel engines, and found that there is a strong association between water soluble organic carbon (WSOC), organic acids, and DTT. The DTT consumption rate per PM mass was correlated with the WSOC ($R = 0.94$, $p < 0.001$) and sum of organic acids ($R = 0.81$; $p = 0.05$) contents of PM. WSOC is a complex mixture of a diverse group of semi volatile species, including dicarboxylic acids, poly acidic compounds, polyethers etc. (Decesari *et al.*, 2000).

Fig. 10 compares the mass and number-based semi-volatile PM fraction and the redox activity from different diesel engine particle samples (Biswas *et al.*, 2009). As shown in the figure, there is remarkable reduction in redox activity as the aerosols are denuded of their semi-volatile fraction, and with the exception of one vehicle (operating without any control technologies) over 80% of the overall particle redox activity is found in the semi-volatile PM fractions (Biswas *et al.*, 2009).

Atmospheric dilution directly affects the particle volatility distribution by shifting the gas-particle

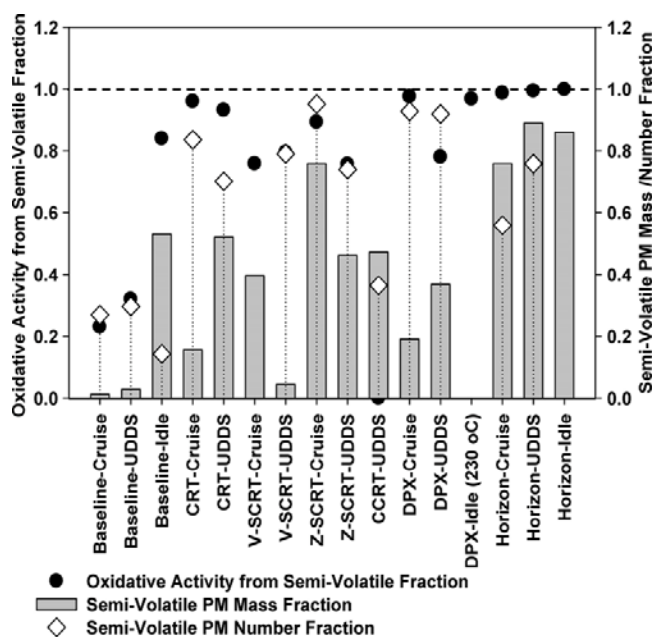


Fig. 10. Relationship between redox activity and semi-volatile PM fraction. Reprinted from Biswas *et al.*, (2009) with permission from ACS.

partitioning process of semi-volatile species. As we discussed in the previous section, the fraction of these semi-volatile species bound to the PM phase may affect their toxicity, at least in the context of their ability to produce oxidative stress and cellular injury. Biswas *et al.* (2009) reported particle redox activity data measured at various locations, where vehicle emissions were the major sources of ambient aerosols, including road tunnel environment with dilution ratios of 200 to 300, and ambient environment with dilution ratios in the range from 1500 to 4000. Fig. 11 shows the redox activity expressed in DTT consumption rate with respect to the atmospheric dilution ratio (Biswas *et al.*, 2009). The PM redox potential very clearly decreases with increasing atmospheric dilution (thus decreased semi volatile components present in the PM phase) until it reaches a lower threshold value of ~ 0.02 n-moles/min/ μg of PM.

These observations corroborate the results reported from dynamometer tests, i.e., that an increased semi-volatile PM fraction tend to induce higher overall redox activity on a per PM mass basis. These findings further illustrate the significant role of semi-volatile aerosols in determining PM toxicity. Due to the association of dilution ratio and PM volatility, atmospheric dilution conditions may thus play a neglected yet important role in determining PM effects on human health and in assessing public exposure to combustion-generated aerosols in the atmosphere. The authors would like to point out that the investigation of the health effect of volatile PM compositions as reviewed in this paper is a new area in the frontier research of particle toxicity. The current findings have called for the attention of the significance of PM volatility and its impact on public exposure. However, further in-depth studies are still needed to investigate the mechanism of PM toxicity.

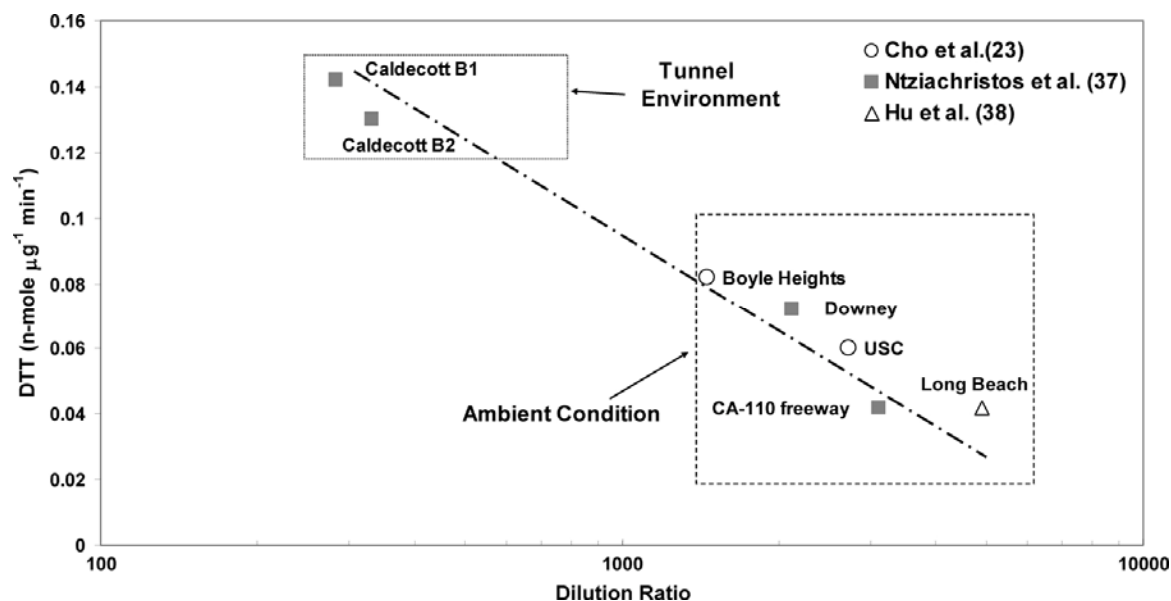


Fig. 11. Redox activity from various studies with respect to atmospheric dilution ratio.

Note: CRT: Continuously Regenerating Technology; SCRT: Selective Catalytic Reduction combined with Continuously Regenerating Technology; V-SCRT: Vanadium based SCRT; Z-SCRT: Zeolite based SCRT; DPX: Diesel Particulate Trap with catalytic wash-coats; CCRT: Catalyzed Continuously Regenerating Trap; UDDS: Urban Dynamometer Driving Schedule. Reprinted from Biswas *et al.* (2009) with permission from ACS.

SUMMARY AND DISCUSSION

Summary

Combustion generated aerosols, especially vehicular PM emissions, are the dominant sources of ambient aerosols in the urban atmosphere. Upon emission from the vehicle tailpipes, the gas-particle mixture of exhaust undergoes various atmospheric dynamic processes, which change the physical and chemical characteristics of the ambient aerosols. These processes include dilution, nucleation, coagulation, evaporation and possible re-condensation of organic vapors onto pre-existing PM, all of which control the dynamics of the exhaust mixtures shortly after their emissions from vehicles.

From vehicle tailpipe to ambient environment, dilution plays a key role in characterizing the exhaust aerosols. Non-labile PM components, such as black carbon, trace elements and metals and high molecular weight organic tracers, are mostly affected by dilution; their atmospheric concentrations are a function of the degree to which the exhaust is diluted by atmospheric dispersion and mixing. Cooling of the exhaust during dilution also enables the formation of nucleation particles from gaseous precursors, and changes the number concentrations and size distribution of the emitted aerosols. For semi-volatile species, increased dilution also shifts the gas-to-particle partitioning process towards the gas phase, and alters the PM volatility and chemical composition of the emitted aerosols as they reach the ambient level.

With the presence of photo oxidants in the atmosphere, gas phase volatile organic compounds (VOCs) participate in the photochemical reactions and form secondary aerosols via different pathways. In addition to the VOCs,

the formation of secondary organic aerosols (SOA) is also significantly enhanced by the photo-oxidation of organic vapors evaporating from semi-volatile PM during ambient dilution, resulting in the different diurnal patterns of primary and secondary organic aerosols.

Semi-volatile PM contains a wide variety of organic compounds and their fraction in the total PM determines their overall toxicological potency, thus their ability to induce adverse health effects. Recent toxicity studies have shown a direct correlation between the semi-volatile PM fraction and PM redox activity, indicating the significance of PM volatility in effecting public exposure to ambient aerosols. This relationship is also reflected in the correlation between ambient dilution ratio, which affects the fraction of semi-volatile species in total PM, and their redox activity.

Discussion and Few Recommendations

Current vehicular PM emission standards as well as ambient pollution standards are based on PM mass measurement. However, with the new advancement of emission control technologies and new findings in PM toxicology research linking adverse health effect with individual PM compositions, there is growing concern about the suitability of such a single metric as the standard for regulation.

Advanced vehicle emission control technologies are effective in reducing solid, non-labile PM emissions by means of filtration. However, recent investigations have shown substantial increases (by one order of magnitude, and often more) of particle number emissions from retrofitted vehicles due to the formation of nucleation mode particles from organic vapors in the exhaust. The

emission of these smaller particles in the atmosphere may pose a greater threat to public health, since they deposit deeper in the human respiratory system and their chemical composition appears to be intrinsically more toxic than the non-labile PM. Europe is adopting a new particle measurement program (PMP), which measures the 'solid' particle ($d_p > 20$ nm) number concentrations from diesel exhaust after removing the volatile PM fraction by heating the exhaust to 300 degree C. In light of recent toxicity findings discussed in our earlier sections, indicating the increased potency and redox activity of the semi volatile nanoparticles, such a measure would seem imprudent.

In ambient conditions, atmospheric processes may significantly change particle size distribution and number concentration by nucleation, condensation, coagulation and secondary reactions. These changes highlight the difficulty and uncertainty in establishing meaningful standards for both vehicle emissions and ambient air quality based on particle number or mass concentrations only. We thus recommend that a better understanding of the linkages between PM size, chemistry and toxicity should be developed in order to adopt regulatory strategies that might be sufficiently protective to the public. Of particular note is the semi-volatile PM from vehicular exhaust because of its unique role in atmospheric processes leading to the formation of secondary aerosols. Moreover, the semi-volatile PM fraction is highly correlated with PM redox activity and its ability to induce oxidative stress, and it is therefore a key determinant of the overall PM toxicological potency. Given the increased toxicity of these semi-volatile species, efforts should be made to reduce their emissions from newer vehicles, including reductions in their gas-phase precursors formed during the combustion process. Atmospheric dilution plays a key role in determining the degree to which these semi-volatile species are partitioned in the particulate phase, thus directly affecting their overall toxicity in the context of public exposure. It is recommended that more research efforts are needed to investigate the dynamics and atmospheric behavior of these semivolatile species. Air quality models and emission inventories will need to account for PM volatility distribution and their evolution in the atmosphere with photochemical aging. The work of Robinson *et al.* (2007) is an excellent starting point in addressing these complex processes.

We also recommend that current emission testing procedures should be modified to reflect real-world conditions in characterizing PM emissions and evaluating their impacts of ambient exposure. Considering the impact of temperature on the semi-volatile PM fraction, the current strategy of diluting vehicle exhaust with particle free air at elevated (and mostly uncontrolled) temperatures needs to be seriously re-considered. We suggest that emissions testing should be conducted ideally with the inclusion of a range of dilution temperatures (e.g., at least 2–3 settings between 0 to 30 degrees C to cover typically encountered ambient conditions in most urban areas). The effect of atmospheric aging also needs to be taken into consideration in characterizing emissions under realistic

conditions.

In summary, current mass-based PM emission regulations and ambient air quality standards will need to be re-considered to address the emerging literature findings on physico-chemical and toxicological characteristics of combustion-generated aerosols. New metrics, such as particle number concentrations, chemical composition and PM volatility will need to be considered in attempting to develop a better understanding of the adverse health consequences of public exposure to these aerosols. Current emission testing procedures also need to be modified to reflect the impact of atmospheric processes on combustion-generated aerosols in the real-world conditions.

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