Seasonal differences of the atmospheric particle size distribution in a metropolitan area in Japan

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We measured the particle number concentrations as a function of distance from road.

The particle number concentrations were observed to be decaying with distance.

The decay rate depended on season and particle diameter.

The spatial distribution of <30 nm particles strongly depend on seasonal temperature.

Mass-transfer theory suggests it is due to evaporation of semivolatile materials.

Abstract

We compared the effect of ambient temperature observed in two different seasons on the size distribution and particle number concentration (PNC) as a function of distance (up to ~250 m) from a major traffic road (25% of the vehicles are heavy-duty diesel vehicles). The modal particle diameter was found between 10 and 30 nm at the roadside in the winter. However, there was no peak for this size range in the summer, even at the roadside. Ambient temperature affects both the atmospheric dilution ratio (DR) and the evaporation rate of particles, thus it affects the decay rate of PNC. We corrected the DR effect in order to focus on the effect of particle evaporation on PNC decay. The decay rate of PNC with DR was found to depend on the season and particle diameter. During the winter, the decay rate for smaller particles (<30 nm) was much higher (i.e., the concentration decreased significantly against DR), whereas it was low during the summer. In contrast, for particles >30 nm in diameter, the decay rate was nearly the same during both seasons. This distinction between particles less than or greater than 30 nm in diameter reflects differences in particle volatility properties. Mass-transfer theory was used to estimate evaporation rates of C20–C36 *n*-alkane particles, which are the major *n*-alkanes in diesel exhaust particles. The C20–C28 *n*-alkanes of 30-nm particles completely evaporate at 31.2°C (summer), and their lifetime is shorter than the transport time of air masses in our region of interest. Absence of the peak at 10-30 nm and the low decay rate of PNC <30 nm in diameter in the summer were likely due to the evaporation of compounds of similar volatilities comparable to the C20–C36 *n*-alkanes from particles near the exhaust pipes of vehicles, and complete evaporation of semivolatile materials before they reached the roadside. These results suggest that the lifetime of particles <30 nm in diameter depends on the ambient temperature, which differs between seasons. This leads us to conclude that these particles show distinctly different spatial distributions depending on the season.

Keywords: Nanoparticles; Diesel exhaust particle; Particle number concentration; PM_{2.5}; Exposure assessment; Evaporation

1. Introduction

Atmospheric air quality standards regulate particulate matter with diameters of 2.5 μm and smaller ($\text{PM}_{2.5}$) based on their mass concentration. Nanoparticles, that is, particles with a diameter (D_p) of less than 50 nm (Kittelson, 1998), in diesel exhaust are included in, but contribute minimally to, $\text{PM}_{2.5}$. Despite their minor contribution to $\text{PM}_{2.5}$, nanoparticles have drawn increasing attention because of their toxicity and associated health risks (HEI, 2002; Oberdorster et al., 2005). Nanoparticles are potentially toxic because their deposited dose in terms of number of particles is higher than that for larger particles. This is because the number concentration of nanoparticles in urban environments is considerably higher than that of larger particles (Kumar et al., 2010), with the highest alveoli deposition for particles 10–20 nm in diameter (ICRP, 1994).

A major source of nanoparticles in the urban atmosphere is diesel-fueled vehicles. Thus, various studies have measured nanoparticles (modal diameter range of 20–30 nm) from diesel engines (Kittelson, 1998; Shi and Harrison, 1999; Vaaraslahti et al., 2004) and in the urban roadside atmosphere (Shi et al., 1999; Molnar et al., 2002; Charron and Harrison, 2003; Hasegawa et al., 2004; Kumar et al., 2008a). Nanoparticles are formed in the exhaust pipes by nucleation during cooling of hot exhaust over 100 $^{\circ}\text{C}$ (Kubo et al., 2005). It is hence expected that nanoparticles are emitted from exhaust pipes to atmosphere regardless of ambient temperature because exhaust temperature is much higher. In addition to primary emission from diesel vehicles, the nucleation also occurs in the roadside atmosphere during the cooling of semi-volatile gases from vehicle exhausts (Charron and Harrison, 2003; Janhall et al., 2004). Therefore, both nanoparticle concentrations and total particle number concentrations (PNCs) are highest nearest roadways and have been shown to decrease according to an exponential or a power law with distance from a road (Shi et al., 1999; Zhu et al., 2002; Pirjola et al., 2006). During transport, the pollutant plume is diluted by the ambient air, and various physical and chemical processes change its chemical composition, physical characteristics such

as size distribution, and concentration in the air (Morawska et al., 2008; Kumar et al., 2010). Thus, to assess the exposure in terms of PNs, it is insufficient to measure only the total PNCs because the deposition efficiency of inhaled particles depends strongly on the particle size, and the size distribution changes spatially. Instead, the spatial distribution of size-resolved PNCs should be determined.

The fate of nanoparticles emitted from diesel engines may also depend on the ambient temperature, because diesel nanoparticles are composed mainly of organic compounds. In particular, in laboratory studies, the branched alkanes and alkyl-substituted cycloalkanes from unburned fuels or lubricating oils that contribute most to the diesel nanoparticle mass (Tobias et al., 2001) have been shown to evaporate easily when heated (Sakurai et al., 2003). The dilution factor modifies the gas-particle partitioning (Pankow, 1994), and so it also affects the organic carbon (OC) content of diesel nanoparticles (Fujitani et al., 2009, 2012) by affecting evaporation to the gas phase. Evaporation of nanoparticles has also been observed in the ambient environment. For instance, Biswas et al. (2007) investigated the volatility of ambient particles at 10 and 150 m downwind from a major highway using a Tandem Differential Mobility Analyzer equipped with a heater (60 and 110 °C). They found that particles 20 nm in diameter were largely volatile at both distances, whereas larger particles (>40 nm) showed evidence of external mixing. In general, the nonvolatile fraction increased with particle size. Fushimi et al. (2008) compared the organic composition of particles 30 to 60 nm in diameter between a roadside and a background site in Japan in the winter and reported that organic compounds from lubricating oils were present at both sites, and some of the C33 *n*-alkane and more volatile organic compounds had partially evaporated in the atmosphere after emission from diesel vehicles. Thus, both field (Fushimi et al., 2008) and laboratory (Fujitani et al., 2009, 2012) studies have shown that diesel nanoparticles evaporate easily at ambient temperature. A recent study by Dall'Osto et al. (2011) supports our hypothesis as they also reported the loss of traffic produced nanoparticles by evaporation, rather than coagulation process, from the air that was aged during less

turbulent conditions in urban area.

Thus, diesel nanoparticles have a short life span, and the spatial distribution of PNCs in the vicinity of a road is likely to vary depending on the particle size, ambient temperature, and atmospheric dilution. In this study, we measured size-resolved PNCs, particle masses, and NO_x concentrations as a function of distance from a major road (up to ~250 m) in the summer and winter. Measurements are made at different spatial locations away from the road during both seasons and results are discussed to identify probable causes of seasonal differences in particle size distributions.

2. Methods

2.1 Site description

Measurements were conducted around a traffic intersection in Kawasaki City, Kanagawa Prefecture, Japan, where a main highway, “Industrial Road,” crosses another road (Fig. 1). Kawasaki City has a population of about 1.4 million and its air quality is considered to be heavily polluted by traffic emissions. Size-resolved PNCs, suspended particulate matter, gaseous pollutants (e.g., NO_x), and meteorological parameters have been measured continuously at a long-term monitoring site near the intersection since 2003. Industrial Road is 30 m wide (7 traffic lanes), and the Metropolitan Expressway is elevated about 5m above the Industrial Road. The average traffic volume during the weekday at this intersection is approximately 52,000 vehicles per day; about 25% of which are heavy-duty diesel vehicles. A residential area lies northwest of the intersection. Most buildings along Industrial Road have two stories, having average height of about 7.5 m. Further details of the measurement site can be seen in Hasegawa et al. (2004).

2.2 Data acquisition

For this study, total and size-resolved PNCs, NO_x, PM₁₀, PM_{2.5}, elemental carbon (EC), and OC were measured for short periods during two summers (3–5 August, 2009, 16–18 August, 2010) and three winters (2–4 February, 2009, 1–3 February, 2010, and 31 January to 2 February, 2011). All

measurements were conducted on weekdays during the same time periods: 0600–0800, 0800–1000, 1500–1700, and 1700–1900 local time.

Measurements were made for 1 h along a mobile measurement path from A1 to A7 (mobile measurement A) and at four stationary points along the path (Fig. 1). Two of the four stationary points were roadside sites (“Intersection” and “Road side”), and the other two were background sites (“Nakadome Park” and “South of Park,” which are 168 and 180 m perpendicular away from the edge of Industrial Road, respectively). Along a second mobile measurement path (mobile measurement B), measurements were made for 10 min at each of the 10 sampling points, located from 1 to 201 m perpendicular away from the Industrial Road (Fig. 1). The order of measurements was from 18 m to 201 m on the road I, and from 1 m to 88 m on the road II. The instruments used for the measurements, their specifications, and the sizes of the measurement data sets are listed in Table 1. Five sets of instruments were used in parallel at the four stationary sites and for mobile measurement A. Each set consisted a condensation particle counter (CPC 3007, TSI, Shoreview, MN, USA) for measuring PNCs from 10 nm and larger in diameter and two size-resolved personal aerosol samplers (SIBATA Scientific Technology, Soka, Saitama, Japan). The Engine Exhaust Particle Sizer (EEPS, 3090, TSI) used for mobile measurement B measured size-resolved PNCs based on their electrical mobility diameter (D_m) in the 5.6–560 nm range. The high time resolution (up to 10 Hz) of the EEPS allows its use under non-steady-state conditions. The GPS-logged data (longitude and latitude) were converted into perpendicular distances from the edge of Industrial Road. The EEPS and NO_x analyzer (APNA-360, HORIBA, Kyoto, Japan) were calibrated daily following the manufacturer’s instructions.

The instruments used for mobile measurements were mounted on carts (Canyon, Tokyo, Japan) (Fig. S1). These carts were moved manually along the paths so that no exhaust emissions would be generated by their movement. The air sampling inlets of all instruments were about 1 m above

ground level, and sampling tubes were not used to avoid any possible diffusion losses within the tubes (Kumar et al., 2008c). For mobile measurement A, CPCs and the size-resolved personal aerosol samplers were powered by self-contained batteries; their exhaust was particle free because the filters removed all the particles. For mobile measurement B, four lead batteries (SEB100, GS YUASA, Tokyo, Japan) and an inverter (HG-350, Cellstar, Yamato, Kanagawa, Japan) supplied AC power to both the EEPS and NO_x analyzer (Fig. S1). Approximately 2-m-long tubes were connected to the EEPS and NO_x analyzer exhaust ports for discharging their exhaust just above the ground level; this arrangement was used to minimize the resampling of the exhaust emissions.

Mobile measurements A and B both began and ended at the long-term monitoring site situated at the intersection. In addition, the CPCs used for the stationary site were gathered at the long-term monitoring site before and after each measurement. Therefore, ambient concentration measurements made by all instruments just before leaving or just after their arrival at the long-term monitoring site were compared against simultaneous measurements made by the scanning mobility particle sizer (SMPS) and the NO_x analyzer at the long-term site to check for differences in instrument output. Total PNCs measured by all five CPCs were usually within the acceptable limit of 10%. We therefore corrected each CPC count for any systematic deviation from the average value in order to cancel out instrumental differences, and then we report here the average of the counts made by the five CPCs. Before the field measurements, we measured the CPC concentrations in the laboratory and compared these results with those from a laboratory electrometer (3070A, TSI); these differences were also within 10% ($R^2 \approx 1$). Moreover, we compared the PNCs measured with the CPCs and the EEPS for this study with the PNCs measured using the two SMPSs (3034 and 3936, TSI) at the long-term monitoring site (Supplementary Figs. S2 and S3). The modal diameter in the EEPS measurements tended to be smaller than that obtained with the SMPS (Fig. S3). For particles larger than 10 nm in diameter, the total PNCs measured by the EEPS were about 30% smaller than those measured by the

CPCs (Fig. S2). We used the EEPS data without any correction. NO_x concentrations obtained by the analyzer used for this study and by the instrument at the long-term monitoring site agreed well (within 5.4%; $R^2 = 0.95$) (Fig. S4).

We used size-resolved personal aerosol samplers to collect PM_{2.5-10} and PM_{2.5} samples, which were analyzed for particle masses, EC contents, and OC contents. The particle mass was obtained by determining the increase in the mass of a TX filter (TX40HI20-WW, Pall, Pine Bush, NY, USA) after sampling using an electric microbalance (UMX 2, Mettler-Toledo, Columbus, OH, USA; readability 0.1 µg) equipped with a charge neutralizer (Am-241) in an air-conditioned room maintained at a constant temperature of $23 \pm 0.2^\circ\text{C}$ and a relative humidity of $50 \pm 1\%$. The EC and OC contents collected on quartz fiber filters (2500QAT-UP, Pall) were quantified by means of a carbon analyzer (model 2001, Desert Research Institute, Reno, NV, USA) using the IMPROVE protocol (Chow et al., 2001). Total carbon (TC) was calculated as the sum of EC and OC.

3. Results

3.1 Meteorology and traffic data

Hourly traffic volume was about 3100 ± 230 (average $\pm$ standard deviation) vehicles during the day hours (0600 to 1900 h) and 1100 ± 620 vehicles during night hours (1900 to 0500 h). Hourly heavy-duty traffic volume was about 780 ± 160 vehicles during the day hours and 280 ± 140 vehicles during night hours. Our long-term monitoring site data of PNCs in the 10-30 nm size range show a positive correlation with heavy-duty traffic volume ($R^2 = 0.28$). This suggests that the PNCs at the long-term monitoring site were affected by primary emissions. Because of the steady traffic volume during the day, we expected emissions to be nearly identical among these four daytime periods. Moreover, differences in concentration of pollutants between the time periods were within the variation in each period, and we therefore merged the data obtained during these time periods before analysis. The temperature during the measurement periods in the summer and winter were $31.2 \pm 3.6^\circ\text{C}$ and 6.6

$\pm 2.8\text{ }^{\circ}\text{C}$, respectively. Figs. 2a–b show wind rose diagrams of 1-min averaged values obtained during mobile measurement A in summer and winter. The wind speed and direction were measured at 3 m above the road level at the long-term monitoring site. The average wind speed was $1.07 \pm 0.45\text{ m s}^{-1}$ in summer and $0.69 \pm 0.33\text{ m s}^{-1}$ in winter. Winds were predominantly from the northeast and north in summer and winter, respectively. Industrial Road is oriented 41° north of east; therefore, the wind mainly blows parallel to the road in summer and perpendicular to it in winter.

3.2 Effect of wind on the spatial distribution of PNCs

Several studies have shown that wind speed and direction affect the spatial distribution of PNCs. For instance, Hitchins et al. (2000) reported that the concentration of ultrafine particles decays to around half its maximum concentration at a distance of 100–150 m when the wind is blowing normal to a road, and at a distance of 50–100 m when the wind is blowing parallel to the road. They also reported that the wind has no effect on total PNCs at distances greater than 15 m from the road when the wind is blowing toward the road. Further, Zhu et al. (2002) showed that PNCs at 30 m downwind from a freeway depended on wind speed when the wind direction was within 45° of normal to the freeway.

To analyze the effect of wind direction on the PNC spatial distribution, we categorized the CPC data obtained at each distance from Industrial Road according to the wind direction at the time of measurement (Figs. 2c–d). The CPC data were obtained every second during mobile measurement A (solid lines in Fig. 1) about 50 m from the north–south road, and were averaged over 10-m distance intervals from Industrial Road. Winds were grouped into the four directions shown in Fig. 2a; wind directions 1 and 3 are perpendicular and directions 2 and 4 are parallel to Industrial Road. Very few data were obtained for direction 3 during the summer (Fig. 2c) or direction 2 during the winter (Fig. 2d), and those data are therefore not shown in the figures.

Irrespective of wind direction, PNCs were the highest at the roadside and decreased with

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increasing distance from the road. During summer, differences in PNCs at each distance away from the road insignificantly depended on wind direction as indicated by the standard deviations shown in Fig. 2c. During winter, PNCs near the road apparently depended on the wind direction, but the PNCs measured when the wind was blowing parallel to the road did not differ from those obtained when the wind was blowing toward the road (Fig. 2d). PNCs were relatively higher in the area leeward from Industrial Road during wind direction 3 because higher PNCs were measured on the north side of Industrial Road than on the south side. On the other hand, PNCs were higher on the south side of Industrial Road during wind direction 1. When the wind blew from Industrial Road toward a sampling point (direction 3) on the north side, the measured PNCs within 150 m of the road were higher than those measured during other wind directions. Beyond 150 m, PNCs were independent of wind direction and concentrations were similar ($\text{ca. } 4 \times 10^4 \text{ cm}^{-3}$) to those measured on the south side when the wind direction was opposite (direction 3) or parallel (direction 4) to the road. This value is the background PNC during winter. When the wind blew from the road to the sampling point (direction 1) on the south side, higher PNCs were measured relative to other wind directions even at 150 m from the road because the exhaust plumes passed through an open space (a park) without becoming dispersed.

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We did not categorize mobile measurement B data according to wind direction or speed because the frequency of wind direction 3 during winter was low (8.7% of total data) and the wind speed was low during these measurements in both summer and winter (see Section 3.1). Both traffic- and wind-produced turbulence and any mean flow that might result from the influence of traffic and wind can affect the magnitude and the spatial distribution of PNCs (Kumar et al., 2008b). When wind speed is low, traffic-produced turbulence is the dominant process causing dilution of particles emitted at street level (Di Sabatino et al., 2003; Solazzo et al., 2007). Kumar et al. (2008b) showed that PNC differences caused by wind turbulence are small when wind speed is below 1.2 m s^{-1} for

particles in the 10–300 nm range. During our study, the average wind speed was lower than this value.

3.3 Particle number and size distributions as a function of distance from the road

Figure 3 shows the size distributions measured at various perpendicular distances from the north edge of Industrial Road. During the winter, the modal diameter (D_m) was 10–30 nm at a distance of 1 m from the road, but the concentration of 10–30-nm particles suddenly decreased at about 19 m from the road. During the summer, a large peak between 10 and 30 nm was absent at a 1 m distance from the road; instead, the distribution was bimodal, with peaks at 10 nm and around 40–60 nm. The shape of the distribution at distance of 1 m from the road was significantly different between both seasons (Fig. S5a). As the distance from the road increased, the peak heights decreased (Figs. 3a, c), but the distribution shape was almost maintained in the summer (Fig. S5b). On the other hand, in the winter, the distribution shape changed, such that there was a relative decrease in the PNCs 10–15 nm in diameter at a distance greater than 19 m from the road and for 15–30 nm at a distance greater than 95 m from the road compared to at a distance of 1 m from the road (Fig. S5c).

During mobile measurement B, both the PNCs and NO_x concentrations decreased with increasing distance from the road (Figs. 4a, b). The initial decrease was steep out to 50 m and then became gradual. By fitting a power-law function to the total PNCs during the summer and winter as a function of distance [dist.] from the road, we obtained the following relationships: $\text{Total PNC}_{\text{summer}} = 1.07 \times 10^5 \times [\text{dist.}]^{-0.189}$ ($R^2 = 0.79$), and $\text{Total PNC}_{\text{winter}} = 2.02 \times 10^5 \times [\text{dist.}]^{-0.337}$ ($R^2 = 0.73$). These equations indicate that the roadside concentration was about 1.89 times higher during the winter than during the summer, and the exponents of the fitted equations indicate that the decay rate with distance during the winter was about 1.89 times higher than that during the summer.

Similar data were obtained for each season during two measurement years (Figs. 3–6), suggesting that the measurement periods were representative of the season. For this study, the measurements were made during the hottest and coldest months in Japan; therefore, the data represent

only the extreme conditions. The PNCs depend on specific weather conditions, and correlated well with temperature in our long-term measurement. Consequently, we anticipate that measurements in other months of the year with a different temperature profile would be within the range of the results obtained during these two extremes.

Similar seasonal PNC differences have been reported previously. For instance, Zhu et al. (2004) reported that near a freeway in Los Angeles, the PNCs of particles with diameters in the 6–12-nm range in the winter were about twice those in the summer, and that PNCs decayed more slowly as a function of distance from the road in the winter (23.2 ± 4.0 °C) than in the summer (30.3 ± 3.7 °C). Likewise, Pirjola et al. (2006) showed that PNCs at a roadside in Helsinki in the winter were about 2.1 times more than those in the summer, and that the average PNC decreased by 39% in the winter (-15.6 to 5.3 °C) and by 35% in the summer (14.1 to 18.4 °C) at 65 m downwind from the road when the wind blew perpendicular to the road.

3.4 Particle number and mass concentrations at various points near the roadside

We compared particulate pollutants between the summer and winter at the two roadside and two background sites as well as during mobile measurement A, pooling data of the different measurement years (Table 2). The $PM_{2.5}$ at the roadside sites slightly exceeded the Japanese national $PM_{2.5}$ daily standard value of $35 \mu g m^{-3}$. Even at the background sites, the $PM_{2.5}$ and PM_{10} were similar or higher than the World Health Organization guidelines for 24-hour mean values which are $10 \mu g m^{-3}$ and $50 \mu g m^{-3}$, respectively (WHO, 2006).

The PNCs, $PM_{2.5}$, PM_{10} , and EC concentrations were higher at the roadside than at the background sites, suggesting that these pollutants had a traffic source and were affected at the roadside in both seasons. The roadside-to-background total PNCs ratios were highest (1.4 and 2.5 in the summer and winter, respectively), followed by the EC ratios in both size ranges (1.4–1.8) and the $PM_{2.5}$ and PM_{10} (1.2–1.4). The spatial distribution of the PNCs was more variable than that of

particle masses, in accordance with the findings of Kaur et al. (2005), who emphasized that it is important to evaluate both mass and number concentrations to assess urban air quality in relation to human exposure. Concentrations obtained by the mobile measurements were nearly in the middle to those obtained at roadside and background sites, except for the OC concentrations. In both size ranges, the OC concentrations in mobile measurement A were higher than the OC concentrations measured at the roadside and background sites, which were similar to each other. These results indicated that there were other sources of OC besides on-road traffic. These other sources of OC might include restaurants selling grilled meat near mobile measurement path A. However, our analysis of the PNCs data obtained by the CPCs during mobile measurement A indicated that these sources were a minor contribution to the PNCs compared with vehicles on Industrial Road.

4. Discussion

4.1 Seasonal differences in the spatial distribution of size-resolved PNCs

4.1.1 Dilution ratio of roadside atmosphere

Our results, reported in Section 3.3, are comparable to previous observations by Zhu et al. (2004) and Pirjola et al. (2006), who also found that the roadside PNCs were about twice as high in the winter as in the summer. In winter, atmospheric conditions are generally stable and the height of the mixing layer is low that can lead to reduced atmospheric dilution. In addition to low atmospheric dilution in winter, since low temperatures promote condensation and suppress evaporation, the negative correlation between roadside PNCs and temperature is expected. Hence the PNC spatial distribution (i.e. the decay rate of PNC) is also expected to differ between the summer and winter. To cancel out the effect of dilution and to focus on the effect of particle evaporation on the PNC spatial distribution, we determined dilution ratios with atmospheric air at our study site by dividing the roadside NO_x concentrations by the NO_x concentration at various distances from the road, after subtracting the background concentration (Fig. 4c). We also assumed that vehicles on Industrial Road

were the only source of NO_x and that significant losses due to chemical reactions or deposition of NO_x did not occur in our region of interest at the temporal scale of our study. The lifetime of NO₂ is about a day (Seinfeld and Pandis, 1998) in a typical urban environment, and the lifetime of NO_x should be longer than that of NO₂. Further, Kondo et al. (2008) calculated the lifetime of NO_x during the daytime from OH concentrations in the metropolitan areas in Japan to be 6–10 h in the summer and 25–39 h in the winter. We estimated the transport times of air masses from the roadside to the most distant measurement site (200 m) by using average wind speeds (see Section 3.1) to be notably less in both summer (3.1 min) and winter (4.8 min) than the NO_x lifetimes estimated by Kondo et al. (2008). These results reasonably support our use of NO_x as an indicator of atmospheric dilution. The dilution ratio increased with distance from the road during both seasons (Fig. 4c), and it was higher in the summer, which suggests that vertical mixing is promoted by the greater height of the boundary layer in summer than in the winter.

4.1.2 Seasonal differences in evaporation rate of nanoparticles

We compared total PNCs with the NO_x-based dilution ratios (Fig. 5a) and found that the PNCs decreased as the dilution ratio increased, although the decay rate differed between summer and winter. The PNC decay as a function of the dilution ratio [DR] was well fitted by the following power functions: Total PNC_{summer} = $9.0 \times 10^4 \times [\text{DR}]^{-0.26}$ ($R^2 = 0.80$), and Total PNC_{winter} = $1.9 \times 10^5 \times [\text{DR}]^{-0.61}$ ($R^2 = 0.83$). These R^2 values are slightly larger than those obtained for the power functions based on distance, indicating that the dilution ratio is a better predictor of the PNCs than the distance from the road in our case. The exponents of the fitted equations indicate that the decay rate was about 2.4 times higher in the winter than in the summer when seasonal difference of the atmospheric dilution ratio is cancelled out.

Seasonal difference in the decay rate may relate to particle transformation processes such as changes in particle size and losses due to evaporation and coagulation, as well as the degree of mixing

with background aerosols, which are particle-size dependent. Therefore, we examined the size-resolved PNC decay for both seasons against the dilution ratio in three size ranges: (i) total PNCs in the 5.6-560 nm range (Fig. 5a), (ii) PNCs in the 17.7-20.5 nm size range (referred to as 20-nm; Fig. 5b), and (iii) PNCs in the 115.0-132.8 nm range (referred to as 124-nm; Fig. 5c). Note that these decay rates were determined by using the net PNCs in selected size bins. These net PNCs implicitly assume that evaporation causes a downward shift into smaller size bins and the coagulation an upward shift into larger size bins. Steep slope indicates a rapid decrease in PNCs in certain size bins with the increased DR. The decay rate of the power function fitted to the 20-nm data was steeper during the winter (-0.66) than during the summer (-0.28), whereas the decay rate of the function fitted to the 124-nm data was the same (-0.34) during both seasons. Interestingly, despite a systematic difference of the PNCs for particles with a diameter of 124 nm between the two seasons, the decay rate is the same when the seasonal difference of atmospheric dilution ratio is cancelled out.

We similarly determined the power function decay rates for each particle diameter over the entire measured size range, and then plotted the obtained decay rates against the midpoint diameter of each size bin by season and year (Fig. 6). This exercise was performed for comparing the relationships of the PNC decay rates with particle diameter and ambient temperature at the same DR. The distribution of the decay rates showed different patterns for particles <30 nm in diameter and those >30 nm in diameter (Fig. 6). For particles <30 nm in diameter, the decay rates were steeper during the winter than during the summer, when they were nearly flat, whereas for particles >30 nm in diameter, the decay rates were nearly identical during both seasons. This distinction between particles less than or greater than 30 nm in diameter presumably reflects differences in particle properties in relation to temperature, in particular, the volatility of particles <30 nm in diameter. In contrast, particles >30 nm in diameter showed nearly identical decay rates during both seasons because they were mainly composed of nonvolatile materials (soot particles and urban background

accumulation mode particles), and thus were not affected by the changes in ambient temperature.

At the roadside long-term monitoring sites, nuclei-mode particles contain organic compounds from the lubricating oil of vehicles, and some organic compounds in the atmosphere evaporate even in the winter, while EC is the major constituent (up to 72% of TC) for particles >30 nm in diameter (Fushimi et al., 2008). Further, diesel particles smaller than 30 nm in diameter are generally composed of easily evaporated material (Kittelson et al., 2006), and OC constitutes the major part (79–80%) of nanoparticles (diameter 10–32 nm) in diluted diesel exhaust (Fushimi et al., 2011), as opposed to particles with diameters in the 40–60-nm range, which consist mainly of non-evaporative materials (Ronkko et al., 2007). Thus, our observations are consistent with the results reported in the literature. Sulfur content in fuel has been found to influence nanoparticle formation in laboratory studies (Shi and Harrison, 1999; Vaaraslahti et al., 2004). Studies have reported reductions in roadside or kerbside PNCs after the introduction of sulfur free diesel fuel in European countries (e.g. Wahlin et al., 2001; Jones et al., 2012). In Japan, sulfur free fuel (about 6ppm) has been shipping since 2005 and our measurements covered a much latter period (i.e. 2009–2011) when no sulfur related changes were made to fuel. This proportion of sulfur content is anyway independent of season and hence the sulfate-derived nanoparticles are unlikely to affect our measured PNCs differently during the sampling periods.

To estimate the lifetimes of pure *n*-alkane particles, the change in particle size with time for particles of C₂₀–C₃₆ *n*-alkanes is calculated using the evaporation/condensation equations (see Eqs. S1-7) for a single spherical particle (Zhang et al., 1993). The C₂₀–C₃₆ *n*-alkanes are the major *n*-alkanes in diesel exhaust particles (Schauer et al., 1999; Morawska and Zhang, 2002; Fushimi et al., 2011; Fujitani et al., 2012). Further, the 30-nm diesel particles were a mixture of compounds that had a range of volatilities comparable to C₂₄–C₃₂ *n*-alkanes (Sakurai et al., 2003), and the abundance of the peaks was the largest for the C₂₄ *n*-alkane in roadside environment particles ($D_p = 28\text{--}56$ nm) in

the winter (average temperature of 8.5°C) (Fushimi et al. 2008). The C20–C28 and C20–C24 *n*-alkanes of 30-nm particles completely evaporate at 31.2°C (summer) and at 6.6°C (winter), respectively (Fig. 7), and lifetimes of these *n*-alkanes particles might be shorter than the transport time of air masses in our region of interest (see Section 4.1.1). However, in the real world, complete evaporation would not occur because diesel nanoparticles contain nonvolatile materials such as trace metals and nonvolatile organics as well as semivolatile organics (Fushimi et al., 2011). It is expected that the particle size would decrease due to evaporation of semivolatile materials from particles, and subsequently only nonvolatile particles smaller than the original size would be left.

In the summer, the absence of the peak (10–30 nm) at a distance of 1 m from the road (Figs. 3a, c, S5a) was likely due to the evaporation of compounds of similar volatilities comparable to C20–C36 *n*-alkanes from particles near the exhaust pipes of vehicles, and the evaporation of semivolatile materials such as C24 and smaller carbon numbers of *n*-alkane which had already completed before reaching the roadside. The modal diameter of 10 nm (Figs. 3a, c, S5b) might comprise nonvolatile materials that are the residue of particles after evaporation of semivolatile materials. Consequently is observed a low decay rate of PNC <30 nm in diameter (Fig. 6) and a slight change in the shape of the size distribution as a function of distance from the road (Fig. S5b). In the winter, our estimation indicates longer lifetimes for these *n*-alkanes particles than those in the summer, and evaporation occurs slowly during transport from the roadside sites to the background sites. Thus, our measurement results and the estimation of particle lifetimes suggest that the lifetime of particles <30 nm in diameter depended on the ambient temperature which differed between the seasons, leading to a conclusion that these particles showed distinctly different spatial distributions between seasons.

These results have implications towards the respiratory deposition doses due to the exposure to traffic-emitted during the winter and summer seasons (see details in Supplementary material). Larger deposition doses are expected during winter compared with summer, because of low

1 evaporation leading to high concentrations of nucleation mode particles. For instance, the deposition
2 efficiencies were calculated for adult men performing light exercise (inhaled air volume = $1.5 \text{ m}^3 \text{ h}^{-1}$)
3
4 using the ICRP model (ICRP, 1994) as a function of distance from the roadside and the DR (Fig. S6).
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6 For a DR of 1 at the roadside, the deposited doses were $6.1 \times 10^{10} \text{ h}^{-1}$ and $14.3 \times 10^{10} \text{ h}^{-1}$ during the
7
8 summer and winter, respectively (i.e. 2.35 times higher in the winter than in the summer). These doses
9
10 reached to half of its maximum roadside value at a distance of 41 m from the road in the summer and
11
12 at a distance of 7.4 m in the winter. This notable variation in PNC-based alveolar deposition doses also
13
14 indicates the need to monitor both easy-to-evaporate (i.e. nucleation mode) and nonvolatile particles
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16 for accurate exposure assessment.
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Figure captions

Fig. 1. Schematic diagram of the measurement site and sampling points. The solid and broken lines show the path of mobile measurement A; only the data measured along the solid line were used. The measurement pathway route starts at A1 and ends at A7. Stationary background measurement sites are shown as open stars, and stationary roadside sites as a closed star and a closed circle. Measurements were conducted along mobile measurement path B at each of the numbered sampling points shown as open circles. The numbers indicate the perpendicular distance in meters from the edge of Industrial Road. The order of measurements on road I is from 18 m to 201 m, and from 1 m to 88 m on the road II.

Fig. 2. Effect of wind speed and direction on the spatial distribution of PNCs. Wind rose diagrams of values obtained during mobile measurement A and averaged over 1-min intervals during: (a) summer, (b) winter. Changes in PNCs at perpendicular distance from the edge of Industrial Road for different wind directions during (c) summer, and (d) winter. These plots correspond to the average of all data during measurement period while the error bars indicate the standard deviation of all data. CPC data obtained every second were averaged over every 10 m of distance from Industrial Road. The numbers 1–4 in Fig. 2a indicate the wind directions shown in Figs. 2c–d; bold numbers (0.5–2.0) in Figs. 2a and b indicate wind speed (m s^{-1}). The broken line in Figs. 2a and b indicates Industrial Road, which is oriented 41° north of east.

Fig. 3. Size distributions measured at various perpendicular distances from the north edge of Industrial Road: (a) 3–5 August, 2009, (b) 1–3 February, 2010, (c) 16–18 August, 2010, and (d) 31 January to 2 February, 2011. The plots correspond to the average of all data during the measurement period, while the error bars indicate the standard deviation of all data.

Fig. 4. (a) Total PNC, (b) NO_x concentration, and (c) the dilution ratio (DR) derived from the NO_x

concentration as a function of perpendicular distance from the north edge of Industrial Road.

The plots correspond to the average of all data during the measurement period, while the error bars indicate the standard deviation of all data.

Fig. 5. PNCs plotted against dilution ratios: (a) total PNCs in the 5.6-560 nm range, (b) PNCs in the 17.7-20.5 nm range (referred to as 20-nm), and (c) PNCs in the 115.0-132.8 nm range (referred to as 124-nm). The plots correspond to the average of all data during the measurement period, while the error bars indicate the standard deviation of all data. Please note that the scale of y-axis in each figure shows a different range of PNCs.

Fig. 6. Decay rates of the power function relating PNC to the dilution ratio (i.e., exponents of the power function) plotted against the midpoint diameter of each size bin. Decay rates were derived by a method similar to that shown in Fig. 5.

Fig. 7. Changes in *n*-alkanes particle size due to evaporation with the time at (a) 31.2 °C, and (b) 6.6 °C after their emissions in the atmosphere. At initial time ($t = 0$), particle diameter is assumed to be 30 nm.

Tables

Table 1. Instruments used in this **mobile** study to measure particles and NO_x, sampling frequencies, and data set sizes.

Measured parameter	Device, type, manufacturer	Size range	Sampling frequency			Size of data set (summer/winter)
			mobile A	mobile B	stationary	
Total particle number concentration	Condensation Particle Counter (CPC), 3007, TSI	10-1000 nm	1 s ⁻¹	-	1 s ⁻¹	^{a,b} 14/20
Aerosol mass	SIBATA personal sampler (TX filter)	PM _{2.5} ,	2 h ⁻¹	-	2 h ⁻¹	^a 8/12
Aerosol carbon content	SIBATA personal sampler (Quartz fiber filter)	PM ₁₀				
Position (latitude, longitude)	GPS, WSG-1000, Wintec	-	1 s ⁻¹	1 s ⁻¹	-	^c
Size-resolved particle number concentration	Engine Exhaust Particle Sizer (EEPS), 3090, TSI	5.6-560 nm, 32 bins	-	1 s ⁻¹	-	^{b,d} 5-10
NO _x	APNA-360 ^e , HORIBA	-	-	1 s ⁻¹	-	

^aPer measurement site. ^b Data from one time period (e.g., data from 1500–1700 on 2 Feb 2009) count as one. ^c Same as the CPC or EEPS data set size. ^dPer season. The size of the data set differed among measurement sites. ^e Chemiluminescence NO_x analyzer

Table 2. Concentrations (average $\pm$ standard deviation) of particulate pollutants at the roadside and background sites as well as during mobile measurement A in the summer and winter. Total PNCs were measured with CPCs.

		Total PNC	PM _{2.5}			PM ₁₀		
			PM	EC	OC	PM	EC	OC
			[cm ⁻³]	[μg m ⁻³]	[μg-C m ⁻³]	[μg-C m ⁻³]	[μg m ⁻³]	[μg-C m ⁻³]
Summer	Background	(3.21±1.46)×10 ⁴	32.6±12.3	4.3±2.4	14.0±2.8	55.4±18.4	7.6±4.1	19.0±4.3
	Mobile	(3.78±2.10)×10 ⁴	35.2±12.0	4.3±3.4	18.4±0.6	61.2±24.0	7.3±5.6	24.5±1.0
	Roadside	(4.62±2.07)×10 ⁴	40.3±11.2	7.1±3.2	14.0±2.5	64.5±20.4	10.6±3.9	18.5±3.2
Winter	Background	(5.28±2.25)×10 ⁴	32.9±13.2	4.9±2.5	17.7±7.9	46.9±15.8	6.2±2.7	22.7±7.4
	Mobile	(8.23±6.15)×10 ⁴	36.7±14.1	6.2±2.6	23.1±10.5	54.4±17.5	7.6±3.0	29.5±11.5
	Roadside	(12.95±7.74)×10 ⁴	44.7±14.5	8.9±4.3	21.9±11.3	63.6±18.8	11.1±4.8	29.9±12.7

Figure1

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Supplementary material

Fig. S1. Photograph of the EEPS and NO_x analyzer mounted on four-wheeled carts for mobile measurement B.

Comparison of instruments for measuring particle number concentrations and NO_x

The CPC and SMPS are widely used for measurement of PNCs, but it is rare for an EEPS to be used in the field (e.g., Jacobson et al., 2005; Kittelson et al., 2006; Yao et al., 2006; Minoura et al., 2009). We compared total PNCs and size distributions obtained in a roadside environment with an EEPS with those obtained with CPCs and SMPSs to allow our data to be compared with data from the literature obtained by other instruments. An EEPS determines the PNC from the electrical current collected on a series of electrodes. An inversion algorithm is used to deconvolute the data, to correct for image charges and the time delays in the column, and to convert currents from 22 electrometers

into 32 output size channels (TSI, 2004). First, we compared total PNCs measured with CPCs (>10–1000 nm), the SMPS 3034 (10.4–469.8 nm), and the EEPS (10.8–453.2 nm). Then, to check the concentration of particles with diameter below 10 nm, we also measured total PNCs with the SMPS 3936 (DMA 3085, CPC 3025A, TSI, Shoreview, MN, USA) in February 2011. The sample flow rate was 0.6 L min⁻¹ with a sheath flow of 6.0 L min⁻¹, which corresponds to a measurement size range of 3.2–107 nm. All of these instruments were operated concurrently at the long-term monitoring site. The SMPS 3034 measured PNCs and the particle size distribution every 3 min. This instrument at the monitoring site was equipped with a copper sampling tube (length, 2.7 m; inside diameter, 6 mm) though sampling tubes were not used with the other instruments. As described in Section 2.2, the reliability of total PNCs measured with CPCs was confirmed in the laboratory by using an electrometer. Therefore, we regarded CPC measurements as the standard for evaluating total PNC (Fig. S2a). PNCs measured with the EEPS and SMPS 3034 correlated well with the CPC measurements ($R^2 = \sim 0.9$), but were respectively about 30% and 40% lower. Although inconsistencies in the upper part of the size range among instruments, the results did not skew the CPC concentrations because PNCs of 500–1000 nm particles were low (20–30 cm⁻³) measured with an optical particle counter (KR-12A, RION, Kokubunji, Tokyo) and an Aerodynamic Particle Sizer Spectrometer (3321, TSI) at the long-term monitoring site.

Comparisons of EEPS and SMPS measurements (Figs. S2b–e) showed good correlations in each size range, although the fitted equations differed among the size ranges. PNCs of 11–45 nm (Fig. S2c) and 52–93 nm particles (Fig. S2d) measured by the EEPS were somewhat higher than those measured by the SMPS 3034, presumably because of losses due to deposition inside the sampling tube used with the SMPS 3034 (Kumar et al., 2008). EEPS PNCs for particles larger than 100 nm were lower than SMPS 3034 values (Fig. S2e). EEPS-measured concentrations were comparable to SMPS 3936-measured PNCs at about 10⁴ cm⁻³ for the 6–11 nm size range (Fig. S2b) and they showed a good

correlation for the 52–93 nm size range (Fig. S2d); however, EEPS-measured PNCs for the 11–45 nm size range were 70% lower than SMPS 3936 values (Fig. S2c).

We examined the size distribution of concurrent measurements by EEPS, SMPS 3034, and SMPS 3936 at the long-term monitoring site during winter and summer (Fig. S3). The distribution shapes and the peak sizes of the EEPS and SMPS 3034 measurements agreed well (Fig. S3b). However, although the EEPS generally showed a peak at 10 nm, the SMPS 3034 did not show a corresponding peak (Figs. S3a, c, and d). The concentrations obtained by the EEPS and SMPS 3936 overlapped (Fig. S3e, f), except in the size range between 10 and 50 nm. A peak in that size range in the SMPS 3936 data was not seen in the EEPS data. Though SMPS 3034-measured concentrations were lower than those measured by the other instruments (Figs. S3e and f), the peak diameter was similar between the SMPS 3034 and the SMPS 3936. The EEPS-measured concentrations were 70% lower than those measured by the SMPS 3936 in the range of 10–50 nm (Fig. S2c), which resulted in a smaller peak diameter of 10 nm in the EEPS results compared with the SMPS 3034 data (Fig. S3). We concluded that the peak diameter in the EEPS data tended to be 10 nm smaller than the SMPS peak diameters and that total PNCs of particles larger than 10 nm measured by the EEPS were about 30% smaller than those measured by the CPCs.

Fig. S2. Number concentrations determined by CPC, SMPS 3034, SMPS 3936, and EEPS: (a) total PNCs, and (b–e) PNCs of particles in various size ranges. Each symbol represents data averaged over a period between 15 and 45 min long.

Fig. S3. Size distributions obtained with the SMPS 3034, SMPS 3936, and EEPS. Each symbol represents data averaged over a period between 15 and 45 min long.

Fig. S4. NO_x concentrations determined at the long-term monitoring site and by mobile measurements during this study. Each symbol represents data averaged over a period between 15 and 45 min long. The error bars indicate the standard deviation of all data.

Fig. S5. Size distributions normalized to the total PNC. (a) the distance of 1m from the road in both seasons and various perpendicular distances from the north edge of Industrial Road in (b) summer and (c) winter.

Evaporation of *n*-alkane in particle phase

We used evaporation/ condensation equations of a single spherical particle (Zhang et al. 1993) to calculate the changing particle size (D_p in m) with time (t in sec) as follows;

$$\frac{dD_p}{dt} = -\beta \frac{4D_{ij}M_i}{D_p\rho RT} \times \left\{ p^0 \exp\left[\frac{4\sigma M_i}{D_p\rho RT}\right] - p \right\} \quad (S1)$$

where β can be calculated from Eq. S4, D_{ij} is a diffusivity of vapor species i in surrounding gas j [$\text{m}^2 \text{sec}^{-1}$], M_i is a vapor molecular weight [kg mol^{-1}], ρ is a density of species i in the liquid phase [kg m^{-3}], P^0 is a vapor pressure over a plane surface [Pa], σ is a surface tension of species i [N m^{-1}], R is the gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), T is a temperature [K], and p is a partial pressure of the species far from

the particle.

The vapor pressure over a curved surface will increase for small particles, i.e., the Kelvin effect,

$$\frac{p^s}{p^0} = \exp\left[\frac{4\sigma M_i}{D_p \rho RT}\right] \quad (S2)$$

where p^s is a vapor pressure of the species over a curved surface [Pa].

The evaporation or condensation rate is governed by the Maxell equation,

$$J_c = \frac{2D_{ij}M_i(p^s - p)}{D_p RT} \quad (S3)$$

where J_c is a mass flux in the continuum regime.

We use mass flux J in the transition regime is related to J_c by

$$\beta = \frac{J}{J_c} = \left[1 + \frac{J_c}{J_k} - \frac{1}{\left(1 - \frac{0.52}{E}\right)^{-1} + \frac{6.08\alpha J_k}{J_c}} \right]^{-1} \quad (S4)$$

$$\frac{J_c}{J_k} = \frac{4D_{ij}}{ED_p} \left(\frac{\pi M_i}{2RT} \right)^{0.5} \quad (S5)$$

$$\alpha = (1 + \delta) \frac{3\pi}{8\sqrt{8}} \left(\frac{M_i + M_j}{M_j} \right)^{0.5} \quad (S6)$$

where E is an evaporation coefficient (for the purposes of this study, we assumed this to be unity), M_j is a surrounding gas molecular weight [kg mol^{-1}], $\delta = 0.132$ when $M_i \gg M_j$, and J_k is a mass flux in the free molecule regime.

A surface tension [N m^{-1}] was derived by following equation (Poling et al., 2001),

$$\sigma = KP_c^x T_b^y T_c^z \left[\frac{1-T_r}{1-T_{br}} \right]^m \quad (S7)$$

where $K = 0.158$, $x = 0.50$, $y = -1.5$, $z = 1.85$, and $m = 11/9$ (Poling et al., 2001). The values of P_c , T_b , and T_c were from Lemon et al. (2000).

We calculated D_{ij} , p^0 , and ρ by the SPARC chemical property estimator (EPA, 2011) for C20–C36 *n*-alkanes at 6.6 and 31.2 °C. The changing of particle size with time for particles of the *n*-alkanes was calculated for an initial particle size of 30 nm (Fig. 7). For this calculation, we assumed p to be zero and this would lead to minimum lifetime. For example, the lifetime of C24 *n*-alkanes at 31.2 °C will be longer 1.04 times and 1.21 times when $p = 0.1 \times p^s$ and $p = 0.5 \times p^s$.

Differences in particle number deposited doses between summer and winter

We estimated the deposited doses in the alveolar region in terms of particle number from the size-resolved PNCs and the deposition efficiencies in the alveolar region calculated using the “Simple Code for Aerosols via the Respiratory Route to Estimate Deposition in the Lung” (Suzuki, 2005), based on ICRP models (ICRP, 1994). The deposition efficiencies were calculated for adult men performing light exercise; the inhaled air volume was set to $1.5 \text{ m}^3 \text{ h}^{-1}$. We examined the deposited doses as a function of distance from the roadside and the dilution ratio (Fig. S6). For a dilution ratio of 1 at the roadside, the deposited doses were $6.1 \times 10^{10} \text{ h}^{-1}$ and $14.3 \times 10^{10} \text{ h}^{-1}$ during the summer and winter, respectively (2.35 times higher in the winter than in the summer). The deposited dose decreased with distance from the road; the deposited dose was half its maximum roadside value at a distance of 41 m from the road in the summer and at a distance of 7.4 m in the winter. Thus, the deposited dose varied both seasonally and spatially.

Moreover, the total PNCs and the associated deposited dose in the alveolar region were nonlinearly related. As a result, the seasonal variation in the deposited dose at the roadside differed somewhat from that in the total PNCs, which was about 1.89 times higher in the winter than in the summer (see Section 3.3) because the deposited dose changes when the size distribution is changed.

Environmental standards established based on particle mass concentrations can substitute for the deposited dose because the deposited dose and the particle mass concentration should be linearly related. Most of the particle mass is contributed by larger particles, and their deposition efficiency is approximately constant. Conversely, total PNCs and the associated deposited dose are nonlinearly related because the deposition efficiency depends strongly on the particle size, especially for particles <100 nm in diameter, and particle numbers are generally higher in this size range. Therefore, the total PNCs cannot substitute for the deposited dose, and it is crucial to measure size-resolved PNCs to derive accurate deposited doses.

In most parts of the world, vehicle emission regulations are based on mass-based particulate matter values, except in Europe, where Euro 5 and 6 emission standards regulate the particle number emissions. These standards were based on the recommendations of the Particulate Measurement Program (PMP) launched under the United Nation's Economic Commission for Europe–Group of Experts on Pollution and Energy. Although the present PMP methodology regulates only nonvolatile particles greater than 23 nm in diameter (Kumar et al., 2010), the effect of these regulations on environmental PNCs is of great interest. Continuous monitoring of PNCs in urban atmospheric environments, and vehicle regulations targeting both easy-to-evaporate and nonvolatile particles, will help to considerably reduce PNC-based alveolar deposition doses.

Fig. S6. Deposited alveolar doses in terms of particle number as a function of (a) perpendicular distance from the edge of Industrial Road, and (b) the dilution ratio based on NO_x concentration. Deposition efficiency was calculated for adult men performing light exercise, assuming an inhaled air volume of $1.5 \text{ m}^3 \text{ h}^{-1}$. The plots correspond to the average of all data during the measurement period, while the error bars indicate the standard deviation of all data.

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