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Characteristics of the Nanoparticles in a Road Tunnel

Mitsuhiko Hata[1*], Tong Zhang[2], Linfa Bao[2], Yoshio Otani[1], Yunhe Bai[3], Masami Furuuchi[1]

[1] *College of Science and Engineering, Kanazawa University, Kanazawa, Japan*
[2] *Graduate School of Natural Science and Technology, Kanazawa University, Kanazawa, Japan*
[3] *College of Chemistry and Environmental Engineering, Dongguan University of Technology, Dongguan, China*

ABSTRACT

In a one-way road tunnel with a sidewalk for pedestrians (total length: 667 m, 2 lanes: 7 m width, sidewalk: 3.5 m width), size-fractionated particles that were suspended in the air were sampled and tested for the potential health risks to pedestrians. These particles were predominantly emitted from motorized traffic. Particles down to the nano-size range were collected using a $PM_{0.07}$ sampler based on the "inertial filter" technology, which can be applied for the separation of nano-size particles. PM_{10} and fine particles less than 1 μm were simultaneously monitored online by a tapered element microbalance (TEOM), a condensation particle counter (CPC) and scanning mobility particle sizer (SMPS), and a video camera was used to monitor the amount of traffic and the wind velocity inside the tunnel. Concentrations of mass and polycyclic aromatic hydrocarbons (PAHs) in each size range of particles were discussed relative to the total traffic amount, the types of motorized vehicles, and the sampling duration, and then compared with other data that had been either simultaneously or separately obtained at different sampling locations outside the tunnel.

The correlation was clear between $PM_{0.1}$ and heavy traffic involving large diesel vehicles, such as buses and trucks. The mass concentrations and fractions of PAHs in the road tunnel became larger than at the mouth of the tunnel and the rural sampling site. PM emissions could be classified into fine particles smaller than 0.5 μm and coarse particles larger than 2.5 μm, which referred to exhaust and road dust, respectively. $PM_{0.07}$ particles from vehicle exhaust might have contained a higher component of PAHs.

Keywords: Road tunnel sampling; Nanoparticles; Polycyclic aromatic hydrocarbon; Inertial filter application.

INTRODUCTION

A number of studies have reported the source profiles and the health effects of ambient particulate matters by sizes such as PM_{10} and $PM_{2.5}$ (Seinfeld *et al.*, 1998; Spurny *et al.*, 1999). However, in order to assess the health effects of airborne particulates, it is important to determine the chemical composition of nanoparticles (Maynard, *et al.*, 2007). Because a large proportion of nanoparticles penetrate the lung periphery, i.e., the alveolar region, particles deposited in the alveoli will be quickly dispersed throughout the human body, including infants (Bolch *et al.*, 2001; Semmler-Behnke *et al.*, 2012).

Diesel vehicles are regarded as a main source of nanoparticles in urban and suburban areas. Although much field work has been performed at roadsides and in road tunnels (Marr *et al.*, 1999), the relationship between nanoparticle composition and emission characteristics remains unclear. This is because conventional devices for nanoparticle sampling, such as low pressure impactors such as MSP Nano-MOUDI Cascade Impactor and DEKATI Electrical Low Pressure Impactor (ELPI), have disadvantages in sampling rate, charging efficiency for nanoparticles and the loss of unstable chemicals by evaporation due to a large pressure drop.

Our group has developed a compact Nanosampler (NS), which is capable of the high-speed sampling of particulate matter with an nanoparticle separation (Furuuchi *et al.*, 2010). The advantage of this sampler is a nanoparticle classification with a moderate pressure drop by applying "inertial filter technology" (Otani *et al.*, 2007; Eryu *et al.*, 2009) to reduce significant changes in the components.

In the present study, size-fractionated particles down to a nano-size range that were suspended in a one-way road tunnel with a sidewalk for pedestrians were sampled in order to determine their status and characteristics as well as the health risk potential for pedestrians. The particles were also simultaneously monitored using conventional devices, and a video camera was used to monitor the traffic amount and a mobile weather station was used to monitor the wind

* Corresponding author. Tel.: 81-76-234-4648;
Fax: 81-76-234-4644
E-mail address: m-hata@t.kanazawa-u.ac.jp

velocity inside the tunnel. The concentrations of mass and PAHs in each size range of the particles were discussed relative to the total traffic amount, the types of motorized vehicles, and the sampling duration, then it was compared with other data that had been either simultaneously or separately obtained at different sampling locations outside the tunnel.

METHODOLOGY

Monitoring Sites

Fig. 1(A) shows the sampling locations. Sampling was conducted inside the Sakiura-Wakunami tunnel, which is located on the Kanazawa outer-ring road and is 667 m in total length with a 90 m^2 cross-sectional area for two-lane traffic that is 7 m wide. Fig. 1(B) shows the tunnel cross section. Two different sites were located on the 3.5 m-wide sidewalk inside the tunnel — at the tunnel middle (a) and at the west-side tunnel mouth (b). For comparison, a sampling site (c) was located on the balcony of the 6th floor of a seven-story building in Kanazawa University, 1.3 km northeast from the tunnel. There were no influencing emission sources around site (c) so that it was representative of a sub-urban area influenced by mixed and diluted pollutants that are emitted in an urban area.

Equipment Used

The mass concentrations were continuously monitored using a tapered element microbalance (TEOM) (R & P, Model 1400) with an EPA PM_{10} inlet. For the online monitoring of the number concentrations of fine particles, a condensation particle counter (CPC) (TSI, CPC Model 3007, < 0.1 μm) and a scanning mobility particle sizer (SMPS) (TSI, Model 3080) were used.

Optical aerosol mass monitors (AMM) (MetOne, GT-331, GT-531) were also used for the online monitoring of TSP/PM_{10}/PM_7/$PM_{2.5}$/PM_1. Total suspended particulates (TSP) were collected using high-volume air samplers (HV) (Shibata, HV-500F and HV-1000) for the tunnel and the reference sites, respectively. In order to collect size-fractionated particles in the nano-size range, both at the tunnel and at the reference sites, 2 sets of "Nanosamplers" were developed by the authors (Furuuchi *et al.*, 2010). The Nanosamplers consisted of 4 impactor stages and 1 inertial filter stage (Otani *et al.*, 2007; Furuuchi *et al.*, 2010) and could collect TSP/PM_{10}/$PM_{2.5}$/PM_1/$PM_{0.5}$/$PM_{0.07}$ fractions under a moderate pressure drop (< 30 kPa).

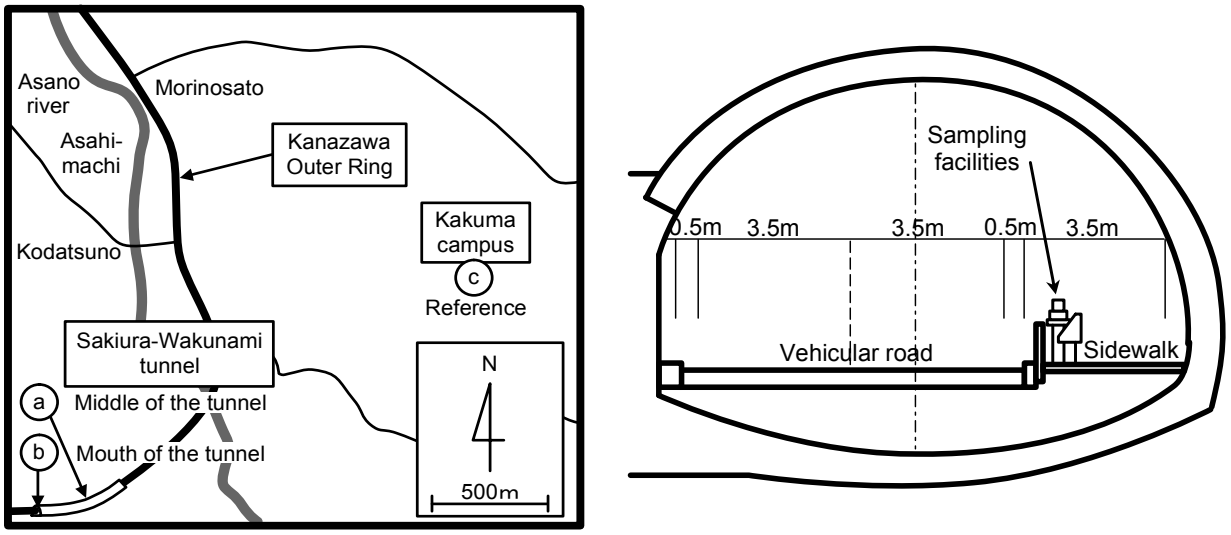
The air flow velocity through the tunnel was monitored by a mobile weather station (Agri-Weather, Weather Bucket®) installed at the site (a) — roadside at a height of 1.5 m. The equipment was calibrated by the manufacturer using a widely used wind monitor (Campbell, CGY-5103). The reported standard deviations of measuring errors were 0.27 and 0.98 m/s, and 7.79 and 14.61° for average velocity, maximum velocity, average wind direction, and direction of maximum wind velocity, respectively. Wind direction, velocity, temperature, humidity, and pressure were recorded at every 10 minutes throughout the sampling period. An anemometer (Kanomax, Anemo-master 6621) was also used for the backup. The traffic through the tunnel was observed at site (a) using a digital video camera to evaluate the traffic amount for each type of vehicle.

Monitoring Period and Duration

The sampling period and duration are summarized in Table 1. In order to discuss the effect of traffic, both of the 15-hour samples, which included morning and evening rush hours and excluded the midnight term, and the full-day sample were performed at site (a) and site (b). The monitoring of particulate matters was continued at site (c) for a year so that averaged data corresponding to the studied period could be used in the following discussion.

Analysis of PAHs

To meet the requirement for negligible filter background for analysis of PAHs, binderless quartz fiber filters (Pallflex



(A) Sampling location map (B) Cross-section of the tunnel

Fig. 1. Sampling locations.

Table 1. Sampling period by Nanosamplers.

Location	Sampling period and weather	Sampling and monitoring devices
(A) Middle of Sakiura-Wakunami tunnel	15h (6:30am–9:30pm), July 22 (Tue), 23 (Wed) and 24 (Thu), 2008 24h (9:30pm–9:30pm), July 22 (Tue)–23 (Wed) and July 23 (Wed)–24 (Thu) (Fine with occasional clouds)	Nanosampler (TSP/PM_{10}/$PM_{2.5}$ /PM_1/$PM_{0.5}$/$PM_{0.07}$) CPC (Number conc. < 1 μm)
	15h (6:30am–9:30pm), June 2 (Tue), 3 (Wed), 2009 15h (6:30am–9:30pm), June 2 (Tue)–3 (Wed), 3 (Wed)–4 (Thu), 2009 (Cloudy with occasional sun)	Nanosampler (TSP/PM_{10}/$PM_{2.5}$ /PM_1/$PM_{0.5}$/$PM_{0.07}$) SMPS (Number conc. < 0.1 μm)
(B) Mouth of Sakiura-Wakunami tunnel	15h (6:30am–9:30pm), June 2 (Tue)–3 (Wed), 2009 (Cloudy with occasional sun)	Nanosampler (TSP/PM_{10}/$PM_{2.5}$ /PM_1/$PM_{0.5}$/$PM_{0.07}$)
(C) Kakuma campus	96h, June 22 (Tue)–26 (Fri), 2008 96h, July 2 (Tue)–6 (Fri), 2009	Nanosampler (TSP/PM_{10}/$PM_{2.5}$ /PM_1/$PM_{0.5}$/$PM_{0.07}$)

2500QAT-UP) were used for sampling after confirming the filter background. Filters were conditioned in a desiccator at ~23°C room temperature and ~50% relative humidity for at least 48 hours, and then initial weights were obtained, which were then used for the sampling. After the sampling, the filters were weighed after 48 hours under the same conditioning procedure. The resultant materials were then analyzed to determine the concentrations of particle-bound PAHs. Sixteen different PAH compounds — Naphthalene (Nap), Acenaphthene (Ace), Phenanthrene (Phe), Anthracene (Ant), Fluorene (Fle), Fluoranthene (Flu), Pyrene (Pyr), Benz[a]anthracene (BaA), Chrysene (Chr), Benzo[e]pyrene (BeP), Benzo[a]pyrene (BaP), Benzo[b] fluoranthene (BbF), Benzo[k]fluoranthene (BkF), Dibenz[a,h]anthracene (DbA), Indeno[1,2,3-cd]pyrene (IDP), and Benzo[ghi] perylene (BghiPe) — were analyzed by HPLC (HITACHI/L-2130/ 2200/2300/2485) using a fluorescence detector and an Inertsil ODS-P column (5 μm, 3.0 mm diameter, 250 mm length) + acetonitril/ultra-pure water mobile phase, after ultrasonically dissolving the samples on the filter in an ethanol/benzene (1:3) solution, followed by evaporation on a rotary vacuum evaporator (Toriba *et al.*, 2003). The average recovery efficiency for 16 components was confirmed to be 0.82 ± 0.12 (n = 3), by adding a standard reagent (Accustandard 0.2 mg/mL in CH_2Cl_2:MeOH (1:1)) to the samples (Tang *et al.*, 2005). The average blank value of the filters was 8.5 ± 5 pg/cm^2 for 2–3 ring PAHs and 5.5 ± 5 pg/cm^2 for 4–6 ring PAHs. These blank values were significantly less than the concentrations of each compound in all samples analyzed.

Although it may not be used in practical applications, the quantity of particles and associated PAHs in particles on the inertial filter for the Nanosampler was also evaluated to determine the separation characteristics. The PAH contamination of the SUS fiber web was also confirmed to be negligibly small — almost the same as those heated to 450°C in an N_2 atmosphere. The inertial filter assembled in the cartridge was conditioned in the same manner with quartz fiber filters, and the same extraction procedure was used.

Those results were discussed based on raw concentration in air, mass fraction in particulate matter and predicted risk evaluation of particles by calculating the toxic equivalent amount to BaP_{eq} from toxic equivalent factors (TEFs).

RESULTS AND DISCUSSION

Characteristics of Traffic and Wind through the Tunnel

The particle emission rate by re-suspension of particles on the road is a function of road conditions, driving speed, vehicle types and wind speed (Sehmel *et al.*, 1980, Nicholson *et al.*, 1993, Goosens *et al.*, 2009). Fig. 2 shows the time changes for 30-minute averages of the total numbers of cars. The trend in the traffic amount was highly reproducible. There were clear peaks exceeding 20 cars/min that corresponded to morning and evening rush hours around 8 a.m. and 6 p.m., respectively. The traffic amount was rather constant during the daytime at around 13 cars/min, and it decreased to a minimum of ~1/10 of the daytime amount between 3 and 5 a.m. Table 1 summarizes the 24-hour averaged fractions for each automobile type. The time changes for 30-minute average numbers of heavy vehicles such as buses, trucks and trailers are shown in Fig. 3. There were peaks in the morning rush hours with no clear peaks appearing in the evening at around 6 p.m., and the traffic amount seemed to peak again in the afternoon from 1 to 3 p.m. This tendency was similar regardless of the sampling date. The 30-minute averaged number fractions of heavy vehicles in Fig. 3 shows a larger fraction from midnight to morning — from 2 to 6 a.m.

Fig. 4 shows the average wind velocity along the tunnel axis, where 99.5% was ± 15 degrees from the axis. The wind always blew from the west to the east of the tunnel. The wind velocity started increasing around 6 a.m. then increased to a broad peak between approximately 1 and 3 p.m. in many cases, and was at its lowest between midnight and 5 a.m. These tendencies were similar regardless of the sampling date since the wind inside the tunnel may be induced mostly by the movement of the traffic. However, the wind velocity in the afternoon seemed to also be influenced by other factors such as weather conditions outside the tunnel and associated influences of tunnel declines from the west to the east entrances.

Behaviors of Particle Concentrations

Fig. 5 shows the relationship of the total number of cars and average PM_{10} concentrations, where data for a small traffic period (9 p.m.–6 a.m.) and for busy traffic periods (6

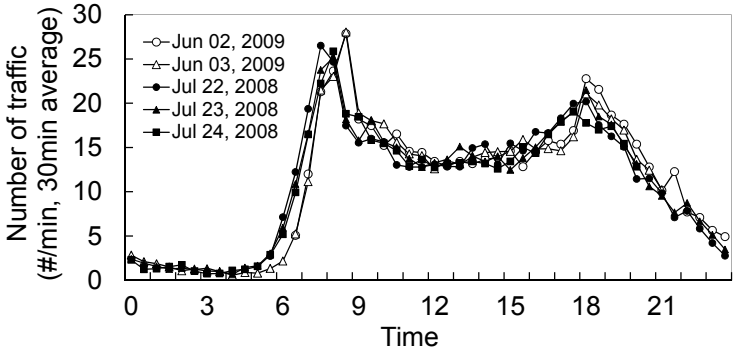


Fig. 2. Total traffic amount through the tunnel (Jul 22–24, 2008 and Jun 2–7, 2009).

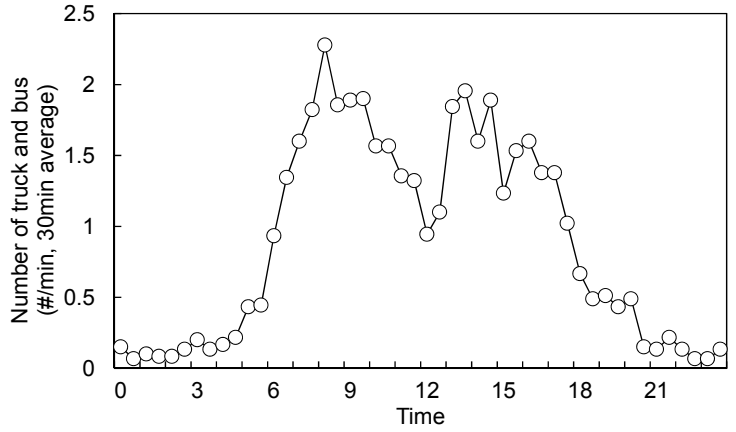


Fig. 3. Traffic amount and fraction of heavy vehicles through the tunnel (Averages for Jul 22–24, 2008 and Jun 2–7, 2009).

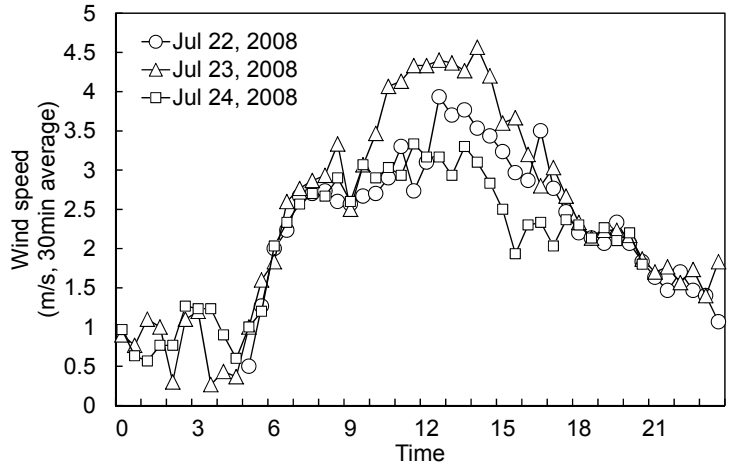


Fig. 4. Time change of wind velocity along the tunnel axis (Jul 22–24, 2008).

a.m.–12 a.m. and 12 a.m.–9 p.m.) are separately shown. Although there were unclear correlations for the left and right ends, with PM_{10} concentrations from 2008 and 2009 that increased on linear regression with traffic amount, with gradients of 1.33 and 1.38, respectively. As described later, particles larger than 2.5 μm dominated the mass fraction in total particles, and may have been mostly road dust that naturally would increase with the traffic amount. From the inconsistency when wind speed was low or high, PM_{10} concentration may have varied depending on not only particle emission from traffic but also dilution by wind from the mouth of the tunnel.

In order to discuss the contribution of diesel emissions to the fraction of fine particles, 30-minute averages of the particle number concentration less than 1 μm and 0.1 μm were measured by CPC in 2008 and SMPS in 2009, respectively. Fig. 6 shows the relationship between those particle number concentrations from CPC and SMPS and

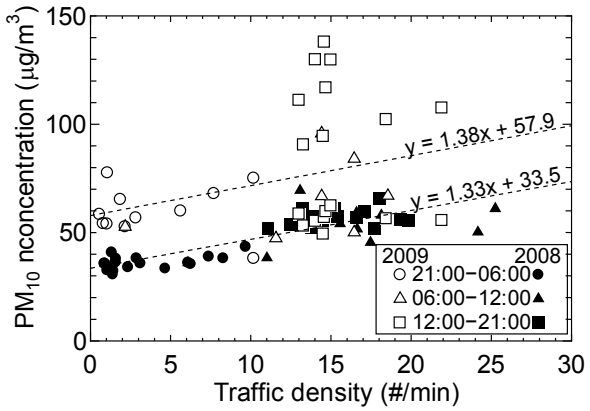


Fig. 5. Relationship between total traffic and PM_{10} mass concentration (Jul 22–24, 2008 and Jun 2–7, 2009).

the number of heavy vehicles. In both size ranges, there were similar linear regressions at gradients of 12,800 and 8,180, respectively. As reported from previous studies (Geller *et al.*, 2006; Biswas *et al.*, 2008), this may indicate a larger fraction of nanoparticles of less than 0.1 μm among the fine particles of less than 1 μm with a predominant contribution of these nanoparticles coming from diesel vehicles. Because the particle concentration varies depend on wind speed as found in Fig. 5, the linear regressions should not be concluded to be similar regardless over years before analysis of further analysis of particle behavior in the tunnel.

PM and PAH Mass Concentrations

Fig. 7 shows the mass concentrations of particles fractionated by a Nanosampler, and the results from 15 and 24 hours of sampling are compared with the data from the referenced location (c). During 15 hours of sampling, the concentrations of particles from 2.5–10 μm had the largest fraction and particles larger than 2.5 mm dominated the total particle mass. Fig. 7(B) shows the mass concentrations of particle-bound 4–6 ring polycyclic aromatic hydrocarbons (PAHs) in each size range from the nanosampler. In contrast with particle concentrations, PAHs at (a) middle of the tunnel increased significantly from (b) mouth of the tunnel and (c) referenced location in fine particles smaller than 0.5 μm and only slightly in those larger than 2.5 μm. This result could represent a difference in the source of the particles — coarse road dust as opposed to exhaust particles.

In order to evaluate predicted risk evaluation of particles by calculating the toxic factor BaP_{eq}, the PAHs concentration normalized to the cancer potency equivalent factor of Benzo[a]pyrene or the BaP Toxic Equivalence. It can be calculated from (Orecchio and Papuzza, 2009) as below.

$$\mathrm{BaP_{eq}} = \sum_i \left(PAH_i \times TEF_i \right) \quad (1)$$

where PAH_i is the concentration of PAH congener i; and TEF_i is the toxic equivalent factor for PAH congener i obtained from Collins *et al.* (1998). As shown in Fig. 8, it is clear that particles ranging from 0.07–0.5 μm in size pose the highest risk and particles larger than 2.5 μm have a low toxicity despite their high concentration. When 15 h and 24 h time courses were compared, particle risk at 15 h was smaller although the mean number of vehicles was 1.4 times greater than that at 24 h. As Fig. 4 shows, wind flow in the night was very weak and unstable, which might have caused a stagnation of the suspended particles.

Fig. 9 shows the estimated PAH emissions based on TEFs by taking a simple mass balance in the tunnel between the 3 sampling sites, (a), (b) and (c), during the 15 h with a high number of vehicles. As shown in the results, the highest amount of the emitted risk from PAHs ranged from 0.07–0.5 μm.

CONCLUSION

In order to discuss the concentrations of mass and PAHs in each size range of particles including nano-size and fine particles relative to the total traffic amount and during heavy use by motorized traffic, ambient particles in a road tunnel were sampled and monitored with traffic amounts and climate status noted.

A clear correlation was found between $PM_{0.1}$ and heavy amounts of traffic that included large diesel vehicles such as buses and trucks. About 10% of the total amount of traffic was considered heavy with different peaks representing the types of vehicles.

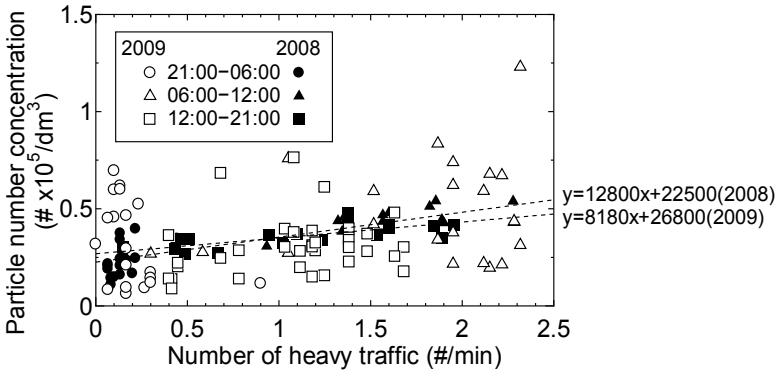


Fig. 6. Relationship between heavy traffic and number concentrations (< 1 μm by CPC in 2008 and < 0.1 μm by SMPS in 2009).

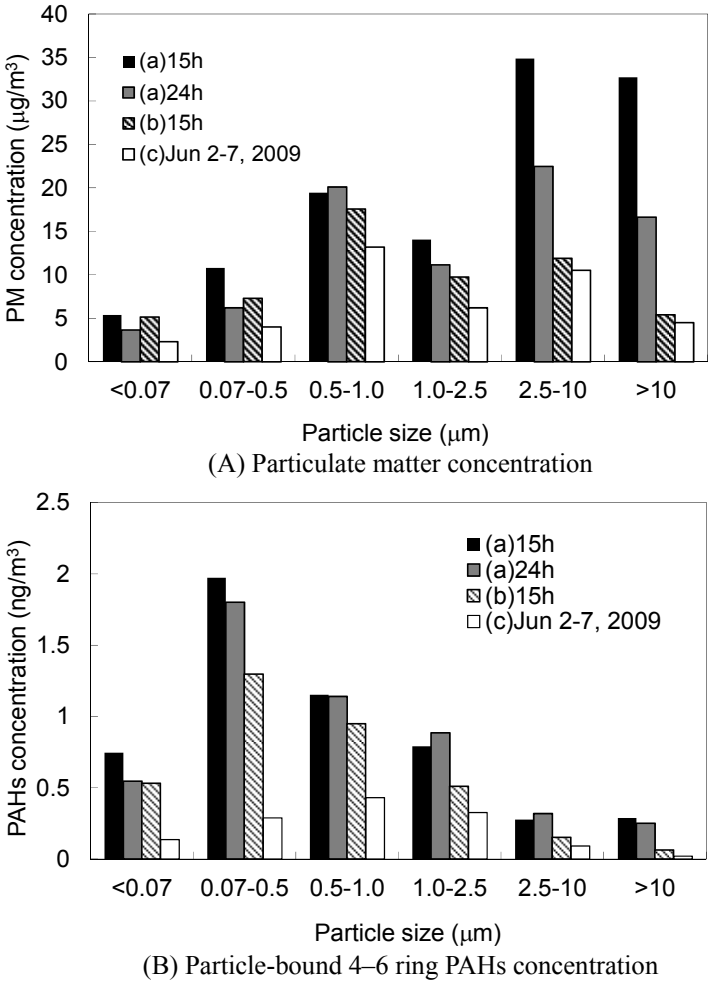


Fig. 7. (A) PM and (B) Particle-bound 4–6 ring PAHs concentrations concentration by size at the (a) middle, (b) mouth of the tunnel and (c) the reference (Jun 2–7, 2009).

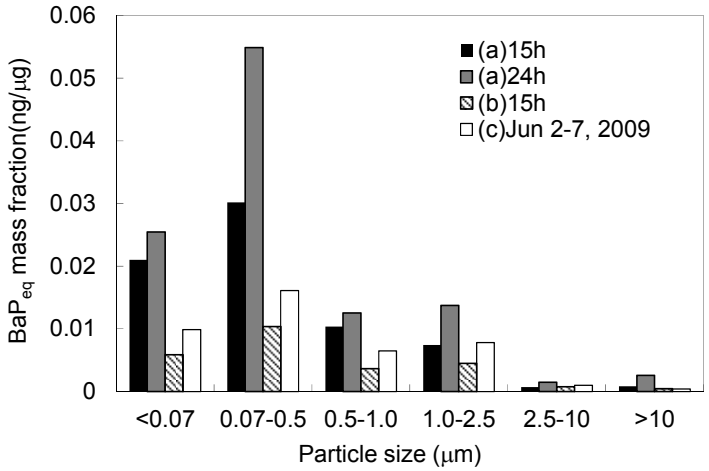


Fig. 8. Estimated toxicity at the (A) middle, (B) mouth of the tunnel and (C) the reference (Jun 2–7, 2009) by using TEFs.

Mass concentrations and fractions of PAHs in the road tunnel became larger than the mouth of the tunnel and the rural sampling site. PM emissions could be classified into fine particles smaller than 0.5 μm and coarse particles larger than 2.5 μm, which referred to exhaust and road dust, respectively. In comparing heavy traffic periods for 15 h with periods of 24 h, the sampling of nanoparticles smaller than 0.07 μm and fine particles that ranged from 0.07–0.5 μm indicated that the nanoparticles from vehicle exhaust contained a high component of PAHs.

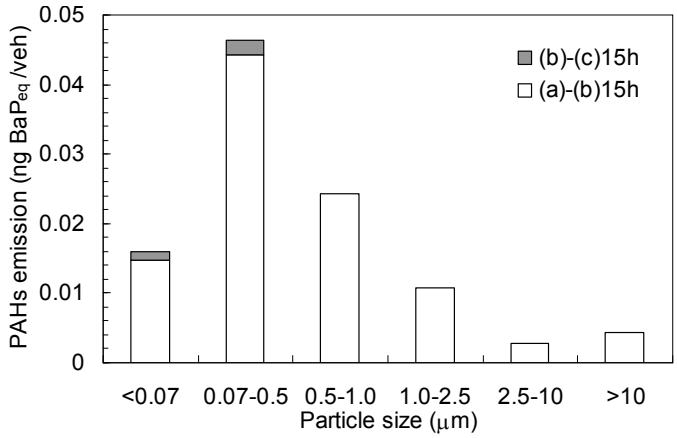


Fig. 9. Estimated PAH emissions based on BaP_{eq}.

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