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Commuter exposure to particulate matter and particle-bound PAHs in three transportation modes in Beijing, China

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ABSTRACT

Exposure to fine and ultrafine particles as well as particulate polycyclic aromatic hydrocarbons (PAHs) by commuters in three transportation modes (walking, subway and bus) were examined in December 2011 in Beijing, China. During the study period, real-time measured median $PM_{2.5}$ mass concentration (PMC) for walking, riding buses and taking the subway were 26.7, 32.9 and 56.9 μg m^{-3}, respectively, and particle number concentrations (PNC) were 1.1×10^4, 1.0×10^4 and 2.2×10^4 cm^{-3}. Commuters were exposed to higher PNC in air-conditioned buses and aboveground-railway, but higher PMC in underground-subway compared to aboveground-railway. PNC in roadway modes (bus and walking) peaked at noon, but was lower during traffic rush hours, negatively correlated with PMC. Toxic potential of particulate-PAHs estimated based on benzo(a)pyrene toxic equivalents (BaP TEQs) showed that walking pedestrians were subjected to higher BaP TEQs than bus (2.7-fold) and subway (3.6-fold) commuters, though the highest PMC and PNC were observed in subway.

1. Introduction

Human exposure to fine particulate matter ($PM_{2.5}$) and ultrafine particles (UFPs) has been associated with increases in mortality and morbidity worldwide (Haberzettl et al., 2012; Sioutas et al., 2005). It was suggested that a 10 μg m^{-3} increase in two-day mean $PM_{2.5}$ was associated with 1.5% increase in total daily mortality (Schwartz et al., 1996). To protect the population from chronic and acute exposure, guideline levels for $PM_{2.5}$ were set to 10 μg m^{-3} (annual) and 25 μg m^{-3} (24-h) by the World Health Organization (WHO, 2006).

Due to rapid economic and population growth, major megacities of China are now facing much greater transportation demand, resulting in increased vehicular emissions as well as air pollution burden. It has been reported that the annual mean mass concentration of $PM_{2.5}$ in most Chinese cities were above 100 μg m^{-3} (Yang et al., 2011). Residents in Chinese megacities are now frequently exposed to high ambient concentrations of $PM_{2.5}$ (Zhao et al., 2009; Zhou et al., 2012), which are much higher than the WHO recommended guideline values and the national ambient air quality standards (NAAQS) for $PM_{2.5}$ in China (with annual arithmetic mean of 35 μg m^{-3}).

Beijing, a megacity with more than 20.69 million residents, has the most extensive and complex traffic system in China. Compared with megacities of other countries, the road traffic situation in Beijing is unique in that streets are filled by a chaotic mix of pedestrians, cars, trucks, buses, bicycles, and other motorized and non-motorized small vehicles. Moreover, vehicle population in Beijing increased significantly during the past 20 years, with a rapid annual growth rate of 13% (Wu et al., 2011) and reached as high as 5.35 million to date. This rapid growth rate in the number of vehicles contributes to increased vehicular emissions in Beijing. There is an urgent need to assess personal exposure to multiple particulate pollutants in traffic related environments in Beijing.

A previous study of Chinese crowd behavior patterns showed that urban residents' average outdoor activity time in Beijing is 3.5 h day^{-1}, and Beijing adult residents spend average 87 min day^{-1} in traffic. In addition, it also pointed out that about 140 million Chinese residents lived within 50 m from roads (MEP PRC, 2013).

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Therefore, urban residents spend considerable amount of time in traffic-related environment each day. Several studies indicated that commuters' exposure to different pollutants was greatly dependent on the choice of commuting (Chan et al., 1999, 2002a, b; Kam et al., 2011a, b). Although a few personal exposure studies related to traffic commuting were conducted in recent years (Du et al., 2011, 2012; Huang et al., 2012; Li et al., 2006, 2007, 2008), they either focused on a certain mode of transportation or on average mass concentrations of gaseous pollutants or inhalable particulate matter (PM). Very few studies have reported information of other important PM pollution parameters (e.g., particulate number concentration, PNC) or its chemical characteristics (e.g., toxic chemical species such as PAHs) which are critical to assess potential health risk.

In this study, personal exposure concentrations of particulate pollutants including fine and ultrafine particles, particle-bound PAHs in three major transportation modes (subway, bus, and walking) in Beijing were investigated with the following objectives: (1) to determine PNC, $PM_{2.5}$ mass concentrations (PMC) and particulate PAH concentrations in different transportation modes in Beijing; (2) to assess time dependent personal exposure concentrations of PM in roadway transportation modes (bus and walking); and (3) to evaluate potential health impact from personal exposure to particulate PAHs. To our best knowledge, it is the first time to investigate multiple particulate pollutants (including chemical composition) in different transportation modes in Beijing.

2. Experimental methods

2.1. Sampling sites

Sampling was carried out between December 10 and 23, 2011 near Peking University (N 39°59′21.13″, E 116°18′25.10″). It is near Zhongguancun, also named as the "the silicon valley" of China. This area is densely-populated (residents, office people and pedestrians) and associated with high flow of vehicles on busy streets. Three commonly used commuting modes (i.e., walking, riding buses, and taking subway) were selected for this study. The walking route (red line in (in the web version) Fig. 1) was along Zhongguancun North Street, which intersects with the 4th ring highway in Beijing. Both air-conditioned (AC) and non-air-conditioned (non-AC) buses were chosen to cover commuters' random choice, with the bus route shown as a green line in (in the web version) Fig. 1. The Beijing subway system includes 10 lines distributed in urban areas and 5 lines in the suburban districts. Two typical lines (line 4 and line 13, black lines in Fig. 1) were chosen with line 4 being an underground line and line 13 being aboveground railway. In other words, subway route was a rectangular loop to cover both the underground and aboveground lines. While part of the straight-line routes of walking, bus and subway was overlapped.

As only one-set of the instruments was available during the field campaign, measurements were made for the walking route in the first period of campaign (December 10–16). Researchers took six 50-min (averaged) round trips each day (every other hour for a trip from 8:00 to 21:00). Each walking trip took place on sections including roadside pavements, skywalks, and road junctions. In the second period (December 18–23), exposure for bus and subway routes was examined. Bus tests were conducted at rush hours and noon (8:00, 12:00 and 18:00). During each 1-h (averaged) round trip, researchers first took non-AC bus and then took AC buses on their way back. And each bus trip included time spent at bus stops, inside the bus, and on the road for back and forth bus transfer. Measurements for subway were conducted in the afternoon (with 1.5 h average time spent for each trip during 14:00 to 16:00). Subway trips usually began with line 4, transferred to line 13, and then back to line 4 (Fig. 1), with data recorded right from entering the subway station entrances. Each trip was made by a minimum of two researchers, each carrying different instruments. This sampling

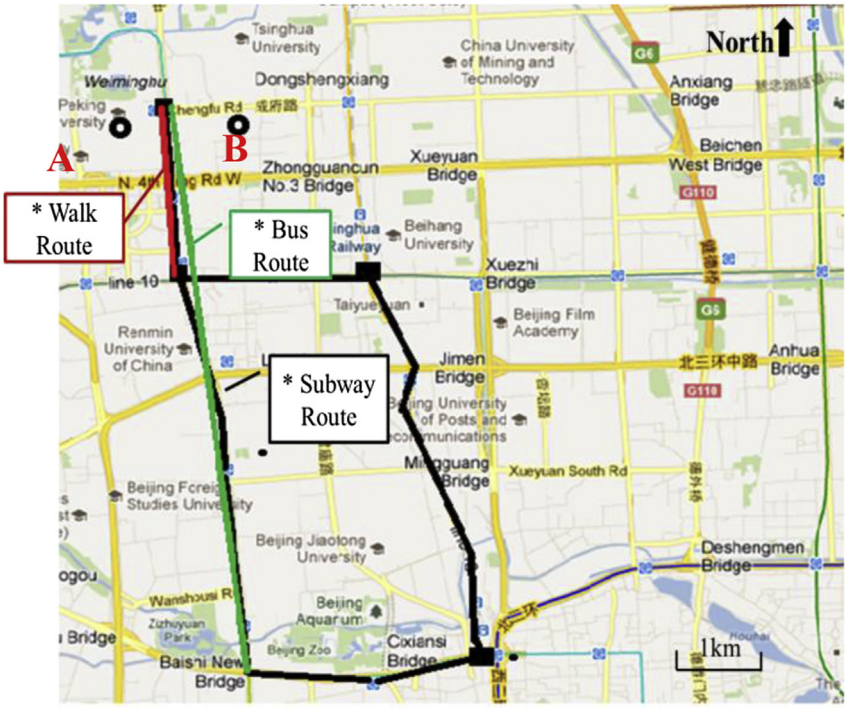

Fig. 1. Map of field sampling routes in this study including walking route (in red), bus route (in green) and subway route (in black). "*" denotes for personal exposure monitoring. "A" indicates the stationary site for measuring ambient $PM_{2.5}$ concentration and "B" shows the site with meteorological information. That is, A and B show the ambient monitoring. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

scheme provided 39 sets of complete valid data for roadside pedestrian, 17 sets of valid data for bus commuters, and 5 sets for subway commuters.

Ambient PMC were measured by a synchronous Tapered Element Oscillating Microbalance (TEOM, Series 1400a, Thermo Scientific Co., Waltham, MA) at a stationary site A (Fig. 1) on the rooftop of a building (about 20 m above ground level) on Peking University (PKU) campus. Meteorological data were measured by the PKU Automatic Meteorology Station B, which is about 400 m away from the stationary site (Fig. 1).

2.2. Instrumentation and quality assurance

A set of portable instruments was used for real-time measurements of exposure levels in the abovementioned public transportation modes. A condensation particle counter (CPC 3007, TSI Inc. St. Paul, MN, 0.7 L min^{-1}) was used for counting total PNC in the size range of 10 nm to 1 μm with 30 s intervals. PMC was measured by a DustTrak Photometer (Model 8520, TSI Inc. St. Paul, MN, 1.7 L min^{-1}) with 2.5 μm inlet and time resolution of 1 min. A Q-trak air quality monitor (Model 8550, TSI Inc., St. Paul, MN) was employed to measure CO_2, relative humidity (RH) and temperature at 30-s intervals. In addition, two parallel personal samplers operated with battery powered Leland Legacy dual diaphragm sample pump (SKC Inc., Eighty-Four, PA, USA, 10 L min^{-1}), were configured to collect integrated $PM_{2.5}$ samples on 37 mm glass fiber filters. All these instrumentations were operated simultaneously.

All instruments were manufacture-calibrated before sampling. Sampling pumps were calibrated with a mini-BUCK air flow calibrator each day. Inlets of all instruments were at approximately 1.5 m above ground during sampling. Testers inside bus and subway train stood away from the door to avoid direct influence by door opening and closing. DustTrak was pre-calibrated against Arizona Test Dust (ISO 12103-1) in the manufacture company (TSI Inc.), and all DustTrak data were corrected against co-located filter based gravimetric measurement at the stationary site with a correction factor of 2.6 (see Figure S1), which also agreed with previous studies (Song et al., 2014; Yanosky et al., 2002).

2.3. PAHs analysis

Glass fiber filters for PAHs analysis were prebaked at 450 °C in a muffle furnace for 4 h before use. Each exposed filter was stored in a Petri dish wrapped with prebaked aluminum foil, and stored in a freezer under −20 °C immediately after sampling.

Personal exposure samples (including five blank samples) were extracted three times with hexane/dichloromethane (1:1, v/v, mixture, Fisher Scientific, Fair Lawn, NJ, USA). Before extraction, d_{10}-anthracene and d_{10}-pyrene were spiked into sample as surrogate standard. The extract was cleaned with 8 mL hexane/dichloromethane mixture (3:2, v/v, Fisher Scientific, Fair Lawn, NJ, USA) through a column packed with 3% water deactivated alumina (0.6 cm i.d. × 6 mm, MP BioMedicals, Solon, OH, USA) and 0.5 cm anhydrous sodium sulfate (Sigma–Aldrich, St. Louis, MO, USA). Then the samples were spiked with deuterium-labeled internal standards (AccuStandard, New Haven, CT, USA) including d_{10}-acenaphthene, d_{10}-phenanthrene, and d_{12}-chrysene and analyzed by a gas chromatography-mass spectrometry (GC-MS, Agilent 7890A-5975C) under electronic ionization mode. A DB-5MS column (30 m × 0.25 mm i.d. × 0.25 μm film thickness; J&W Scientific, Folsom, CA, USA) was used to separate target analytes with 1.0 mL min^{-1} helium as carrier gas. GC operating conditions were as follows: isothermal hold at 70 °C for 1 min, temperature ramp of 8 °C min^{-1} to 270 °C and then 15 °C min^{-1} to 300 °C, isothermal hold at 300°C for 5 min.

Careful quality control criteria were employed to ensure data quality. For each batch of eight samples, one procedural blank sample was prepared. Five field filter blanks were included, and all data presented below were field-blank corrected. Recoveries of surrogate standards were 93.8 ± 16.3% and 96.3 ± 15.9% for d_{10}-anthracene and d_{10}-pyrene, respectively.

3. Results and discussion

3.1. Concentrations of measured pollutants in different traffic environment

Ambient temperature and RH ranged from −6.6 °C to 12.8 °C (averaged 2.6 °C) and 13%–74% (averaged 27%) during the campaign. Prevailing wind direction was from southwest, with an average speed of 1.5 m s^{-1}. In this study, PNC, expressed as number of fine (including ultrafine) particles per cubic meter air, and PMC both varied widely in different transportation modes. Real time monitored PNC ranged from 0.1×10^4 to 4.1×10^4 (median value: 1.1×10^4) cm^{-3} when commuted by walking, 0.03×10^4 to 4.6×10^4 (median value: 1.0×10^4) cm^{-3} by bus, and 0.04×10^4 to 4.1×10^4 (median value: 2.2×10^4) cm^{-3} by subway. Likewise, PMC varied in the range of 3.1–327 (median value: 26.7), 5.0 to 406 (median value 32.9), and 9.6 to 268 (median value: 56.9) μg m^{-3} by walking, riding buses and subway, respectively.

Figure S2 (a, b) presented the overall effect of transportation modes on measured particle number and mass concentrations. High PNC (from 1.5×10^4 to 3.0×10^4 cm^{-3}) was more frequently observed (81%) in subway, which usually occurred at ground entrances of subway stations, on the platform and corridor, might be influenced by air flow exhausted from tunnels due to its air-conditioning and ventilation system. Whilst, for walking and riding buses, lower PNC ($<1 \times 10^4$ particles cm^{-3}) occurred quite often (about 49% for walking and 47% for bus), but bus commuters experienced relatively higher and wide-ranged PNC. Likewise, the most frequently occurring PMC was also higher in subway than that in roadway modes (walking and by riding buses), and two roadway modes exhibited similar PMC profiles. For example, about 67% of the time during the study period, pedestrians and bus commuters were exposed to PMC lower than 50 μg m^{-3}. However, PMC in walking modes had the widest range, and experienced the highest value.

Differences of measured PNC and PMC in the three abovementioned transportation environments indicated different particle sources. Typical PM concentration profiles in each transportation environment were shown in Figure S3, with labels of places where high PM concentrations occurred, e.g. flow roadside snack, road junction, construction site, bus stop, idling, interchange station. For example, up to 1.5-fold increase of PMC could be observed in bus cabins under the idling or stop conditions, and up to 6–7 fold increase of PMC was observed when walking across a road junction. It was noteworthy that, besides vehicular emissions, many roadside sources also contributed to fine particle mass and number concentrations in roadway environments, such as open barbecuing using coal (Hou et al., 2008; Lin et al., 2010), second-hand smoking, construction dust, and street restaurants. About 6–7 fold higher PMC was observed when walking across a construction site. And quick increases in PNC (about 5–8 fold) and PMC (about 5–11 fold) occurred when researchers passed by outdoor barbecue stands or cigarette smokers (see Figure S4).

Trip-averaged concentrations of PNC and PMC in different transportation environments were summarized in Table 1. T-test (with the level of significance defined as $p < 0.05$ (2-tailed)) was performed to compare differences among different commuting modes and different conditions under the same mode (i.e.

Table 1
Particle number and $PM_{2.5}$ mass concentrations in different transportation trips.

Research environment	$PM_{2.5}$ mass concentration (PMC, μg m^{-3})				PM number concentration (PNC,#cm^{-3})				CO_2 concentration (ppm)				Relative humidity (%)				Temperature (°C)			
	N	Ave	Range	S.D.	N	Ave	Range	S.D.	N	Ave	Range	S.D.	N	Ave.	Range	S.D.	N	Ave	Range	S.D.
Railway																				
Subway	5	61.8	40.4–94.4	21.6	5	19,405	16,157-22,395	2914	5	711	331–3828	271	5	22	14.7–38.5	3.6	5	20.5	10.3–24.3	2.1
Ground railway	5	42.4	26.8–80.2	25.3	5	21,740	8451–27,134	7834	5	1379	365–2956	465	5	33.5	16.1–44.3	7.0	5	12.9	6.7–17.9	2.8
Bus																				
Air conditioned bus	17	38.9	6.15–150	26.3	17	21,806	2416–46,049	13,602	17	1402	272–3937	771	17	29.7	10.0–66.6	8.7	17	14.9	−1.5 – 30.7	6.8
Non-air conditioned bus	17	38.4	7.69–99.6	22.1	17	8615	433–35,169	5000	18	1497	263–4528	1030	18	38.0	13.9–86.0	14.8	18	9.0	−5.0 – 16.3	4.4
Roadside																				
Walking	40	49.9	10.5–211	51.7	39	13,924	2857–24,664	5657	38	389	250–3769	274	38	37.3	6.5–85.8	16.0	38	1.5	−8.3 – 14.7	4.1

Note: N stands for sample (or trip) numbers for each transportation mode; S.D. for standard deviation; Ave. for arithmetic mean value.

underground vs. ground subway, and AC bus vs non-AC bus). PMC was higher in underground subway cabins (61.8 ± 21.6 μg m^{-3}) compared with ground railway cabins (42.4 ± 25.3 μg m^{-3}) ($p < 0.0001$). While PNC was much higher in ground railway ($2.2 \times 10^4 \pm 0.8 \times 10^4$ cm^{-3}) ($p < 0.0001$), consistent with the findings of Taipei subway system (Cheng et al., 2012), suggesting higher particle density of underground atmospheric particles (e.g. metals from steel). CO_2 concentration and RH were 2 and 1.5 times higher in ground railway cabins than those in underground subway cabins, suggesting larger numbers of passengers in the ground railway. But higher temperature was found in subway, indicating the difference between open and enclosed microenvironments. Compared with results from previous studies for Beijing subway system, PMC obtained in this study were slightly higher for ground railway transit system (Li et al., 2006, 2007), but 1.5–1.8 times lower for underground subway transit system (Du et al., 2011; Li et al., 2007). Railway transport related PMC in this study were higher than that in other cities, e.g. Hong Kong (Chan et al., 2002a), Taipei (Cheng et al., 2012), and New York City (Morabia et al., 2009; Wang and Gao, 2011), but still lower than that in London (Adams et al., 2001). PNC levels in Beijing subway system were higher than that reported in New York (Wang and Gao, 2011) and Taipei (Cheng et al., 2012). Part of these differences among cities or studies is likely due to differences in emissions, traffic structures, types of vehicles in each city, and seasons when the study was conducted.

Comparable PMC and higher PNC ($p < 0.001$) were found in AC bus compared to non-AC bus in this study (see Table 1), which was different from results reported in Hong Kong (Chan et al., 2002a) and Bangkok (Kongtip et al., 2012). However, it agreed with other studies such as Jones et al. (2006) which reported higher PM_{10} in AC buses compared to non-AC buses and trams in Hong Kong. Kaminsky et al. (2009) found that PNC in-cabin with air conditioning on and windows closed was higher than that with window closed and air conditioning off. In Beijing during winter, AC bus windows were tightly closed, thus air inside cabin was not effectively circulated and filtered. Use of heater core by exchanging heat between coolant and cabin air, might bring in PM from the combustion in the engine and increase PM concentrations in cabins. Routes for air-conditioning and non-air-conditioning buses were quite the same, only with difference in driving directions. According to the sampling records, AC buses experienced a little more idling states compared to non-air-conditioning ones during the trips, and this might contribute to higher PMC and PNC in the former due to the self-pollution from the buses' tailpipe exhaust. The numbers of passengers in non-air-conditioning buses were more than that in air-conditioning ones, which is also reflected by the simultaneously measured higher CO_2 concentrations and RH (Table 1), but its lower interior temperature indicated the cabin was not well tightened or closed. Compared with previous researches in Beijing roadway traffic environment, PMC obtained in this study were comparable for bus commuters and pedestrians (Huang et al., 2012). High standard deviations for both PMC and PNC in roadway traffic (especially walking mode), suggested complex influence from surrounding sources. Pedestrians and bus commuters were under direct exposure to traffic plume especially with long continuous idling fleet and other ground level source emissions (e.g. road dust, industrial dust) on the roadside, whilst re-suspended dust in closed vehicle cabins could also be a major source for $PM_{2.5}$ in buses and subway. It should be noted that, although the number of vehicles on roadway increased significantly during the past few years in Beijing, they are dominated by new types of vehicles which meet much more stringent emission standards.

3.2. Temporal variations of fine PM concentrations in roadway transportation modes

Ambient PMC obtained by gravimetric methods based on offline filter samples collected at the stationary site are presented in Figure S5 to show the regional $PM_{2.5}$ concentrations in the duration of this study. In general, daily PMC was slightly lower during the first seven days for walking mode than that for bus and subway modes ($p < 0.05$), except for the highest $PM_{2.5}$ polluted day

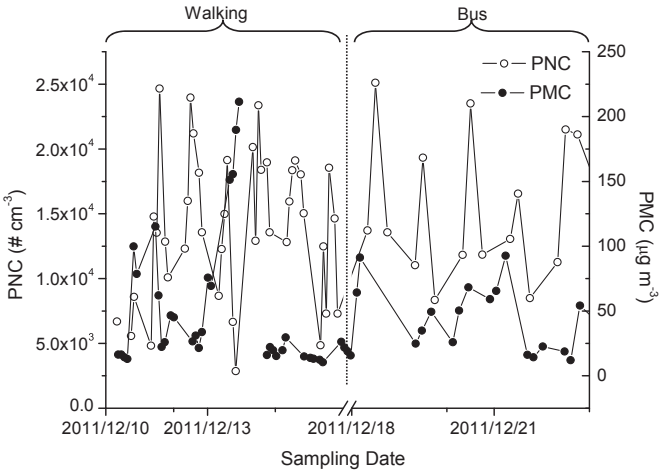

Fig. 2. Temporal variations of trip averaged PNC and $PM_{2.5}$ mass concentration in walking and bus modes during the whole study period.

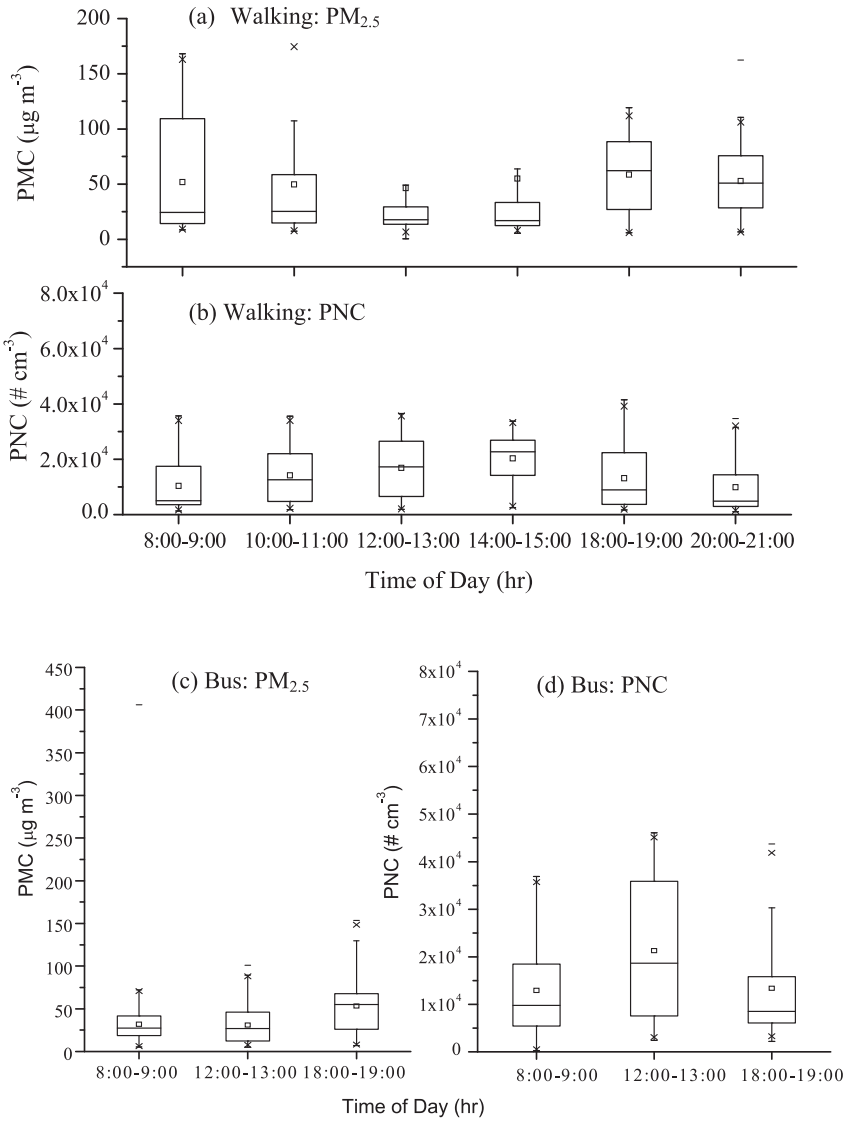

Fig. 3. Temporal variations of exposure level in different transportation modes from 8:00 to 21:00: (a) $PM_{2.5}$ in walking mode; (b) PNC in walking mode; (c) $PM_{2.5}$ in bus mode; (d) PNC in bus mode. The box represents the inter-quartile range (IQR, 25th to 75th percentile) and square indicates mean value.

(December 13th) when $PM_{2.5}$ mass concentration was higher than 200 μg m^{-3}. Temporary variations of PNC and $PM_{2.5}$ levels (averaged by trips) measured in two roadway transportation modes during the two weeks' field experiment (except for December 17, when instruments were not available) are shown in Fig. 2. It should be noticed that, PMC in transportation environment showed large variations compared to PNC, with sharp increase of PMC but slight variation of PNC during high PM polluted days (December 13th), indicating contribution of high PMC but low PNC sources (e.g. dust).

Six trips for walking mode or three trips for riding buses were made at different time periods in each day. Obvious temporal variations of PMC and PNC were found from 8:00 am to 21:00 pm in this study. The highest mean $PM_{2.5}$ concentrations of pedestrians appeared during late traffic peak hours (18:00–19:00) and the lowest occurred during traffic light times around noon (12:00–13:00), which was consistent with those exposed by bus commuters (see Fig. 3a and c), indicating temporal variations of PMC and PNC exposed by commuters and pedestrians were transportation modes independent during this study period. The variation of $PM_{2.5}$ concentrations agreed well with traffic emissions and residential heating caused emissions in winter.

However, PNC exhibited negative correlation with PMC. PNC peaked around noon (12:00–13:00) or early afternoon (14:00–15:00), about 1.5–1.6 times higher than that in the morning and evening traffic rush hours (Fig. 3b and d). Similar results were reported in street canyon in Germany (Voigtländer et al., 2006), rural areas of Austria (Gomišček et al., 2004) and during a summer campaign in southwest Detroit (Young and Keeler, 2004). High PNC but low PMC indicated abundant existence of UFPs, which has also been reported by Young and Keeler, 2004. This might be due to contribution from sources with strong emissions of very fine particles, e.g. cooking and vehicle emission. It is also likely due to attribution from gas to particle conversion especially in the close traffic emission environments during noon time when sunlight is abundant and relative humidity is low (Laakso et al., 2003; Lee et al., 2003; Lovejoy et al., 2004). Nucleation in indoor air has been reported by previous studies (Quang et al., 2012, 2013). All these ambient emitted ultrafine particles or newly formed particles penetrating into bus cabins might lead to the increase of PNC. In addition, the particle size range measured by the portable CPC in this study was from 0.01 to 1 μm, which contributes more to PNC, but not necessarily to $PM_{2.5}$ mass concentration. Temporal variation

of exposure level in subway was not discussed here since only one trip was made each day.

3.3. Inter-comparison among different commuting environments

Physical properties of particles that commuters were exposed to were greatly affected by transportation modes besides exposure time during the day (Huang et al., 2012). Knibbs et al. (2011) reviewed 47 traffic related exposure studies and reported mean PNCs were 4.2×10^4, 4.7×10^4 and 4.9×10^4 particles cm^{-3} for bus, railway, and walking modes, respectively. Chan et al. (2002b) reported that average PM_{10} and CO level in roadway transportation was 1.2–3.0 and 2.6–9.3 times higher than that in subway in Guangzhou. However, in this study, the highest average $PM_{2.5}$ and PNC were both found in subway, which were measured in the afternoon (off-peak hour), when ambient $PM_{2.5}$ were not quite high (See Figure S5). Averaged PMC in subway was comparable to that in walking, but about 1.5 times of that in buses ($p < 0.05$). Meanwhile, PNC was up to about 1.5 and 2.0 times higher than that in walking and buses.

Trip-averaged PM concentrations of overlapped route section from different modes were exclusively selected and calculated. To account for the difference of ambient background levels due to sampling times, ambient concentrations from the rooftop site were also considered. SAS Proc GLM was used to run the following regression:

$$C_e = a + b_a C_a + b_t T + b_i \cdot C_a \times T$$

where C_e is trip-averaged exposure concentration, C_a is averaged ambient concentration during each trip, T is transportation mode (a categorical variable equal to walking, bus or subway), $C_a \times T$ is the interaction of ambient concentration and transportation mode). The Proc GLM outputs for the estimate of each parameter are shown in Table S1. Results show that ambient concentration, transportation mode and their interaction are statistically significant for exposure concentration at the significance level of 0.05. Based on the Pro GLM output, trip-averaged exposure concentration for different transportation modes could be expressed as follows:

$$C_e = \begin{cases} 1.04 \cdot C_a + 6.66 & (walking) \\ 0.79 \cdot C_a + 13.16 & (bus) \\ 0.63 \cdot C_a + 27.82 & (subway) \end{cases} \quad (1)$$

R-square of the model was 0.96. Above model also illustrated influence of ambient air and other sources to exposure concentrations for different transportation modes. The greater intercepts for bus and subway suggested they might have self-pollution, resulting higher exposure than walking when the ambient concentration was low. During this study period, 87% of ambient $PM_{2.5}$ measured in the overlapped route section was lower than 66 μg m^{-3} and only 11% were higher than 97 μg m^{-3}. Based on equation (1), under such ambient PM concentration level, higher pollution level could exist in subway compared with that in walking and buses. In another aspect, trips of subway and walking at the same time period (14:00–16:00) under similar ambient $PM_{2.5}$ level were separately chosen for comparison. Taking December 21st and December 12th for example, ambient $PM_{2.5}$ were both around 40 μg m^{-3}, trip averaged PMC and PNC by walking and subway were 33.7 and 38.2 μg m^{-3}, 2.1×10^4 and 2.1×10^4 cm^{-3}, respectively, also similarly suggesting higher PM concentrations might occur in subway.

Subway cabins were relatively closed microenvironments compared to buses and open streets. During our study, air-conditioning system wasn't operational, piston effect introduced fresh air into the station and exhaust air from the tunnel to outside, resulting in a "cross ventilation effect" and also accumulation of air from tunnels. Therefore, additional sources of fine PM in subway should be considered. For example, particles emitted from mechanical friction might cause high levels of $PM_{2.5}$ (Salma et al., 2007). Kang et al. (2008) reported that particles collected at subway stations were mostly from wear processes at rail-wheel-brake interfaces, and indoor emission sources predominated in the underground subway in Seoul, Korea. About 30% of coarse and fine particulate matter was actually iron particles in subway (Kam et al., 2011a). And more than 100 times higher iron, manganese, and chromium were found in the New York City subway system than in aboveground air (Grass et al., 2010) Besides above factors, date of construction, station depth, the presence or absence of platform edge doors (Grass et al., 2010), passenger volume, ventilation system, and re-suspension of dust from the floor all influenced exposure level and contributed to $PM_{2.5}$ mass.

3.4. Particulate PAHs in different commuting environments

In this study, 19 PAHs (including U.S. EPA priority 16 PAHs) were detected from personal exposure filter samples. For each transportation mode, filters from different trips on the same day were combined as one sample in order to have sufficient mass for reliable GC/MS analysis. Therefore, 6 valid samples for walking, 6 samples for buses and 5 samples for subway were analyzed for particulate PAHs. It is noted that, each sample had one parallel sample and PAHs concentration for each sample was regarded as the average value. Results showed that mean total particulate PAHs exposure concentrations in walking, bus and subway were as 77.8 (range: 22.4–375), 99.6 (49.4–156), 46.3 (16.4–83.3) ng m^{-3}, respectively. These mean PAHs levels were about one or two orders of magnitude higher than that in Los Angeles (Kam et al., 2013). Lower PAHs exposure concentrations in subway might be due to several reasons. First, subway is primarily powered by electricity, which is not a significant source of PAHs. Second, PAHs are mainly present in fine particles (Miguel et al., 2004) while subway is reported to be relatively more enriched in coarse particles (Cheng et al., 2012). Last, the ambient temperature is different between roadway and subway (Fig. 4). Most PAHs are semi-volatile, which can partition between gas and particulate phases depending on the temperature. Higher temperature in subway favors PAHs in gaseous phase (Lohmann and Lammel, 2004; Kam et al., 2013). During our study

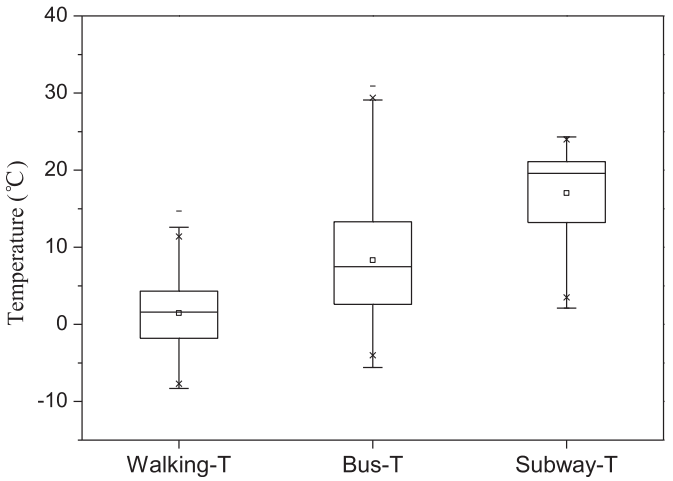

Fig. 4. Commute average temperature in three environments during the sampling periods.

period, temperature in subway was 8–15 °C higher than that in the ambient.

Levels of benzo(a)pyrene (BaP), a marker for carcinogenic PAHs, ranged from 1.44 to 26.5, 3.13 to 10.4, and 0.43–4.59 ng m^{-3} in the study period (8:00 am to 9:00 pm) for walking, bus and subway mode, respectively. It should be noted that, daily mean concentration limit set for BaP is 1.0 ng m^{-3} and 2.5 ng m^{-3} in China's indoor air quality standard (GB/T 18883-2002) and the national ambient air quality standard (GB3095-2012), respectively. Individual BaP toxic equivalent concentration for each PAH specie (BaPeq) was determined by corresponding PAH mass concentration multiplied by the toxic equivalency factors (TEF) according to Nisbet and Lagoy (1992). Toxic equivalents (TEQs) of BaP for total PAHs were the sum of individual BaPeq (∑BaPeq) (see Figure S6). Averaged TEQs for walking, bus, and subway environments were 18.0, 13.3, 5.0 ng m^{-3}, respectively. Apparently, average BaP TEQs concentrations for walking and bus were about 3.6 and 2.7 times higher than those at subway. This is likely due to higher emissions of carcinogen with elevated TEF, e.g. dibenz(a,h)anthracene, indeno(1,2,3-cd)pyrene, Benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(ghi)perylene, etc. in walking environment. Schauer et al. (2002) pointed out that poor combustion spark ignition during idling could generate more benzo(ghi)perylene. Congestion and idling traffic conditions were quite common in Beijing and during this study. It is interesting to note that subway commuters were exposed to the highest PMC and PNC levels, but their ∑BaP TEQs levels of PAHs were relatively low.

Concentrations of PAHs with different rings (from 3 to 6) in three commuting environments are shown in Table S2. Jin et al. (2012) pointed out different number of rings and composition profiles of total PAHs had differential sources and toxicological effects. In this study, PAHs were dominated by 4-ring PAH (50%) in all three transportation modes, followed by 5-ring PAHs (33%). High molecular weight PAHs (5-ring and 6-ring PAHs) were more enriched in walking and bus environment than subway, indicating pedestrians and bus commuters were more subject to vehicular emissions. And these high ring PAHs contributed to higher toxicity of PAHs in roadway transportation due to their high TEFs. Proportion of 3-ring PAHs in total PAHs was much higher in subway compared with walking and bus. According to Fromme et al. (1998), it might be partially attributed to decoration materials. In this study, we speculated that re-suspended dust in subway cabin might play an important role in 3-ring PAHs. Detailed PAHs characteristics in different transportation modes can be found in Zheng et al. (2014). Other chemical tracer analysis (e.g., metal, organic compounds) is needed to determine the sources of particles exposed in different traffic microenvironments.

4. Conclusions

Concentrations of PNC, PMC and PAHs in three primary public transportation modes (walking, bus, and subway) were investigated and compared in Beijing. Walking pedestrians and bus commuters were exposed to a much broader range of PNC and $PM_{2.5}$ mass concentration. Chinese characteristic roadside sources (e.g. outdoor barbecuing and cigarette smoking) contributed to high PM concentrations in roadway transportation environments. Dust might contribute not only to PM concentrations in roadway transportations but also in underground subway. Obvious temporal variations in roadway commuting environments were found with highest PNC appeared around noon while $PM_{2.5}$ peaked in late traffic rush hours. Relatively higher averaged PMC and PNC were observed in Beijing subway system, compared with roadway transportation environments especially in buses. But low PAHs concentrations and toxic equivalents of BaP were found in subway, where 3- and 4-ring PAHs were relatively enriched. Our results suggested that future study should involve detailed chemical tracer analysis and source apportionment tools to provide quantitative source information for particle exposures. And comparisons of different transportation mode in the future study should be improved as exposure considerations should include both time and concentrations.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2015.05.001.

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