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Diurnal variation of nitrated polycyclic aromatic hydrocarbons in PM_{10} at a roadside site in Xiamen, China

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Abstract

Intensive daytime and nighttime sampling was carried out from 23 Oct to 31 Dec 2008 to investigate the occurrence of nitrated polycyclic aromatic hydrocarbons (NPAHs) in PM_{10} at a roadside site in Xiamen, China. At the same time, six PM_{10} samples were collected from a nearby roadway tunnel for comparison. Six NPAHs, namely 9-nitroanthracene, 2- and 3-nitrofluoranthene, 1-nitropyrene, 7-nitrobenz[a]anthracene, and 6-nitrobenzo[a]pyrene, were identified and quantified using GC/MS in negative ion chemical ionization mode. The average total concentration of six NPAHs ($\sum$NPAHs) in the cold season (26 Nov–31 Dec) was 2.3 (daytime) and 9.9 (nighttime) times higher than those in the warm season. Significant statistical difference ($p < 0.01$, 2-tailed) of $\sum$NPAHs between daytime and nighttime was found during both the warm and cold seasons. NPAHs were significantly positively correlated with their parent PAHs and nitrogen dioxide but negatively correlated with ambient temperature. The ratio of 2 + 3-nitrofluoranthene to 1-nitropyrene exhibited a similar diurnal pattern as $\sum$NPAHs and was generally greater than 5, indicating the importance of secondary atmospheric formation. The diurnal variations of NPAHs were all influenced by the diurnal variations of PAHs, nitrogen dioxide, sunlight, and temperature. The daily inhalable exposure to the six NPAHs in the tunnel was much higher than the roadside values in the warm season but only slightly higher than those in the cold season.

Key words: nitrated PAHs; diurnal variations; source; inhalation exposure

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Introduction

Atmospheric nitrated polycyclic aromatic hydrocarbons (NPAHs) are generated as a result of the imperfect combustion of organic matter (Fan et al., 1995; Finlayson-Pitts and Pitts, 2000; Zielinska et al., 2004) or formed via the nighttime reaction of parent PAHs with nitrate radicals (NO_3) and their daytime reaction with hydroxyl radicals (OH) in the presence of NOx (Arey et al., 1986; Atkinson et al., 1990; Atkinson and Arey, 1994, 1997; Reisen and Arey, 2005). For these reasons, they are present in significant concentrations in urban areas as well as in rural and remote areas (Ciccioli et al., 1995; Ciccioli et al., 1996; Tang et al., 2005; Kojima et al., 2010; Minero et al., 2010).

Several NPAHs are believed to be far more mutagenic or carcinogenic than their parent PAHs (Grimmer et al., 1987; IARC, 1989; Durant et al., 1996) and, moreover, are significant direct-acting mutagens and readily condense onto particulate matter due to their low vapor pressure in the atmosphere (Bamford and Baker, 2003; Pedersen et al., 2004). Thus in most cases only particle phase NPAHs are measured, although 2-ring and 3-ring NPAHs (nitronaphthalene and nitroanthracene, nitrophenanthrene)

occur in both the gas and particle phases (Dimashki et al., 2000; Albinet et al., 2007, 2008). Many studies show that NPAHs in vehicle emissions, especially diesel-engine vehicles, play an important role in direct- and indirect-acting mutagenicities (Hayakawa et al., 1997; Zwirner-Baier and Neumann, 1999; Toriba et al., 2007; Yang et al., 2010). Hence, from a human health standpoint, the investigation of NPAHs in emission sources and in ambient air is important (Grimmer et al., 1987; IARC, 1989; Nielsen et al., 1996). Obviously, like many other Chinese cities, Xiamen is undergoing a process of rapid urbanization and rapid economic development, and PM_{10} has been the predominant pollutant for many years, according to the reported data of the Xiamen Environmental Protection Bureau (http://www.xmepb.gov.cn). The total number of licensed vehicles reached 0.27 million at the end of 2008, a year-on-year increase greater than 22%, and the number of vehicles is expected to reach 0.88 million in 2012. Around 29.4% on average of ambient PM_{10} is attributed to motor vehicle emission in Xiamen (Zhang, 2007). Both the direct emission of NPAHs from motor vehicle exhaust pipes and secondary photochemical transformation of PAHs will contribute greatly to particulate pollution in Xiamen. The increase of anthropogenic particulate matter and PAHs in the atmosphere from vehicle emissions has raised health

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concerns in Xiamen (Hong et al., 2007; Wu et al., 2010; Zhao et al., 2010), but to date no data have been reported for NPAHs in the Xiamen atmosphere.

Because of the significant differences of OH and NO_3 radicals, O_3, solar ultraviolet radiation, atmospheric stability (McLaren et al., 2004) and the gas phase reaction pathway of PAHs with NOx between daytime and nighttime, it is expected that NPAHs in the atmosphere should also present a diurnal variation. Some measurements at 12-hr day and night sampling intervals or shorter time periods (4 hr) have been carried out to study the diurnal variations and formation mechanism of NPAHs (Arey, 1998; Reisen and Arey, 2005; Albinet et al., 2007, 2008; Hien et al., 2007; Tsapakis and Stephanou, 2007). Measurements from Ho Chi Minh City show a higher nighttime concentration of 2-nitrofluoranthene (2NF) at two rural sites and a higher daytime concentration at an urban site from July 2005 to March 2006 (Hien et al., 2007). No defined diurnal variation of NPAHs occurred at rural sites in France during either winter or summer sampling (Albinet et al., 2007, 2008). A 6-hr sample collection carried out in central Tokyo in winter showed higher levels of 1-nitropyrene (1NP) in the daytime with respect to those in the nighttime (Ishii et al., 2001). Tsapakis and Stephanou (2007) observed a significant diurnal variation of 2NF and 2-nitropyrene (2NP) at a background coastal site with a maximum during midday (11:00–15:00) followed by a sharp decrease, consistent with the OH radical diurnal pattern during the summer sampling period. However, the highest levels of 1NP and 2NF were observed in the morning (7:00–10:30) during both summer and winter sampling periods in the Los Angeles urban atmosphere (Reisen and Arey, 2005). The above analyses indicate that the diurnal trend of NPAHs in the atmosphere cannot be extrapolated from one setting to another, and depends to a great extent on the specific local atmospheric environment and source strength.

As part of the "Great Xiamen Bay Air Quality Monitoring Project", intensive PM_{10} daytime-nighttime sampling was carried out in autumn-winter 2008 at a roadside site in Xiamen, China. All together 100 samples from the site were studied for NPAHs to characterize the diurnal variation of NPAHs associated with PM_{10} and to investigate the factors influencing their diurnal variations. The roadside measurements can also provide researchers with data to produce health impact assessment reports when evaluating the effect of PM_{10} chemical content on particle toxicity in the air at roadside.

1 Materials and methods

1.1 Sampling and measurements

A coastal roadside site on the roof of the Ocean Building (ca. 21 m height) at Xiamen University (24°26′08″N, 118°05′25″E) in the south of Xiamen Island was selected to carry out the intensive PM_{10} sampling from Oct 23 to Dec 31 2008 using a High-Volume Air Sampler (GMW PM_{10} VOL, Thermo Scientific Co., USA) equipped with a PM_{10} size-selective inlet at a constant flow rate of 1.13 m^3/min. The average daily traffic volume for all vehicles of the road near the sampling site (the distance is ca. 10 m) is more than 20,000 and there is not much difference between weekdays and weekend days. However, the total number for all vehicles in the day is around two times that at night. The number of buses and cars (including taxis) account for 15% and 80% of the traffic volume, respectively. We consider that the diurnal and seasonal patterns of NPAHs in PM_{10} at this roadside site are representative of the roadside general conditions of busy traffic areas in other parts of Xiamen in the presence of similar heavy traffic and vehicle types passing on this road.

For the purpose of comparison, the sampling period was broken into two periods based on the daily temperature, a warm season from 23 Oct to 25 Nov (corresponding to autumn) and a cold season from 26 Nov to 31 Dec (corresponding to winter) (Fig. 1). The daytime samples were collected from 08:00 to 19:00, and the nighttime samples were taken from 20:00 to 07:00 (local time). At the same time, six PM_{10} samples from the Zhonggushan roadway tunnel, near the roadside sampling site, were also collected to investigate the emission characteristics of NPAHs. Because the air was very contaminated in the tunnel, the sampling time was no more than 2 hr in order to prevent overloading of the filters. Glass microfiber filters (GF/A, Whatman, England) were pre-weighed using a microbalance (Sartorius 0.1 mg, Germany) in a temperature (25°C) and humidity (65% RH) controlled laboratory after being baked at 450°C for 4 hr in a muffle furnace. A baked aluminum foil bag was used to store the cleaned filter. After sampling, loaded filters were folded and wrapped in their aluminum foil bags and weighed as soon as possible. The filter samples were stored at –20°C until they were subjected to analysis.

The levels of typical air pollutants, such as PM_{10}, NOx ($NO + NO_2$), SO_2, CO and O_3 (TEOM 1400a, 42i, 43i, 48i and 49i, Thermo Electron Co., USA), from the nearest air quality automatic monitoring station located on the same road within one kilometer of the sampling site, were provided by the Xiamen Environmental Protection Bureau during the sampling time. The meteorological factors of temperature, relative humidity, wind direction and speed, and rainfall were monitored using an automatic weather station (PH-1, XPH Co., China) at the sampling site.
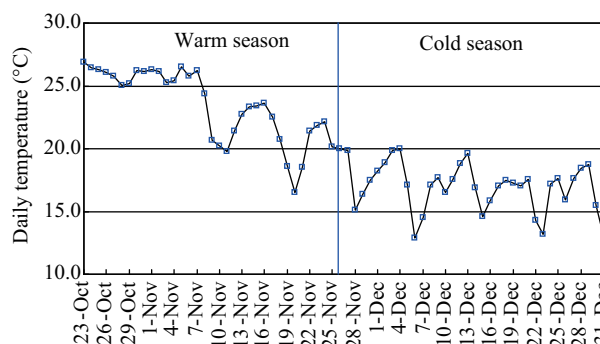

Fig. 1 Daily temperature during the sampling period in 2008.

1.2 Sample analysis and quality assurance

The method of extraction and cleanup was modified from US EPA method 3550B (ultrasonic extraction) and 3630C (silica gel cleanup), Dimashki et al. (2000) and Prvček et al. (2004). A quarter of each filter was cut into small pieces and a known amount of 4-nitro-*p*-terphenyl (AccuStandard Inc., USA) was added to the filters before extraction to serve as a surrogate standard. The filters were ultrasonically extracted three time for 30 min in dichloromethane (DCM) after soaking overnight. All the extracts were merged in a pear-shaped flask and concentrated to ca. ten milliliters by rotary evaporator in a water bath at 20°C under reduced pressure. An additional 15 mL hexane was added into the pear-shaped flask and concentrated again to ca. 1 mL. The concentrated extract was transferred to a silica gel column (1 cm i.d. and 20 cm length with Teflon stopcock) with a pipette and washed with 2 mL of hexane to complete the transfer. The silica gel (type 60, 70–230 mesh, Merk) was pre-cleaned with DCM in the Soxhlet extractor and then activated by heating in a foil-covered glass beaker for 16 hr at 150°C. The column was successively eluted with 25 mL hexane, 40 mL hexane/DCM (6:4, *V/V*) and 30 mL DCM to separate alkanes, PAHs and NPAHs from polar compounds. The fraction eluted by hexane/DCM and DCM was collected together because some target PAHs and NPAHs co-eluted but did not interfere with each other when detected using a different instrument. The PAHs/NPAHs fraction was solvent exchanged to hexane (EPA method 3510) and concentrated to 200 μL using a nitrogen blow-down device, and then divided into two parts for analysis of the PAHs and NPAHs (Pyrček et al., 2004; Wu et al., 2010).

The analyses of NPAHs were performed with a GC/MS (Agilent 6890N-5975B) in negative ion chemical ionization (NICI) and selective ion monitoring mode (Bamford et al., 2003; Reisen et al., 2003; Albinet et al., 2006). An HP-5MS capillary column (0.25 mm i.d. × 30 m, 0.25 μm film thickness, 5% phenyl methyl polysiloxane) was used to separate different compounds and ultra pure helium (99.999%) was used as the carrier gas. The oven temperature program was 70°C (1 min) to 300°C (6.5 min) at 20°C/min. The GC/MS interface temperature was 280°C and electron energy for the mass spectrometer was 70 eV. In the NICI mode, methane (99.999% purity) was used as the reagent gas to minimize molecular fragmentation while allowing ionization of NPAHs by resonance capture of the thermal electrons (Nishioka et al., 1988). The GC/MS in NICI ionization mode can improve the sensitivity of the method by more than two orders of magnitude compared with that of the EI GC/MS method (Bezabeh et al., 2003; Zhang et al., 2010). Standard solutions of 9-nitroanthracene (9NA), 3-nitrofluoranthene (3NF), 1NP, 7-nitrobenz[a]anthracene (7NBaA) and 6-nitrobenzo[a]pyrene (6NBaP) were purchased from AccuStandard and 2-nitrofluoranthene (2NF) was from Chiron. A set of standard mixtures containing the six NPAHs, in concentrations ranging from 1 to 100 ng/mL, were prepared by dilution of stock solutions of

these compounds. It should be noted that 2NF and 3NF were co-eluted from the HP-5MS chromatography column and the two compounds were quantified together when making a calibration curve (Bamford et al., 2003; Albinet et al., 2006). NPAHs in the samples were identified by comparison of retention time with standards and their molecular ions and quantified with the external standard technique. A very good linear relationship was found between the injected amount and measured peak area for each compound ($R^2 > 0.99$).

Field and laboratory blanks were used to determine the potential contamination from transportation, glassware and solvents. Two spiked blanks (standard mixtures spiked into blank filters) were also prepared and analyzed with every batch of samples. Since the recovery rates for each target compound based on spiked blanks were quite different and the surrogate standard of 4-nitro-*p*-terphenyl added to the samples alone could not represent all the target compounds, this surrogate standard was only used to supervise procedure and matrix effects instead of correction for target compound quantification. There was not much difference in NPAHs levels between field and laboratory blanks, and both levels were less than 3% of the mass in samples. Mean recovery rates of the surrogate standards, 9NA, 2+3NF, 1NP, 7NBaA and 6NBaP were 71.3%–92.1%, 85.2%–89.4%, 90.5%–96.0%, 91.1%–93.6%, 90.7%–92.8% and 64.9%–70.2%, respectively. The final results for the six compounds were corrected according to the spiked standards mixtures and blanks. For each compound, the method detection limit (MDL) was determined from the standard deviation of concentration for seven replicate measurements, which was multiplied by the one-sided *t* distribution (the *t* value for a 99% confidence interval is 3.14). The MDL for the air sampling with an air volume of 750 m^3 varied from 0.60 pg/m^3 (9NA) to 1.42 pg/m^3 (7NBaA).

2 Results and discussion

2.1 Seasonal variation of NPAHs

All of the six target compounds were identified and quantified in all the PM$_{10}$ samples. The total concentrations of the six target NPAHs (∑NPAHs) ranged from 37.9 to 802 pg/m^3 during the daytime and from 39.3 to 6195 pg/m^3 during the nighttime sampling period (Table 1), and the levels were one to two orders of magnitude lower than those of their parent PAHs (Wu et al., 2010). The mean value of ∑NPAHs in the roadway tunnel was comparable to that in the nighttime of the cold season at the roadside (Table 1). However, NPAHs profiles in the roadside samples were dominated by 2+3NF, followed by 9NA, while the dominant compound in the tunnel samples was 1NP. The ratio of 1NP to 2+3NF (1NP/2+3NF) ranged from 2.0 to 8.9, significantly higher than those at the roadside (which ranged from 0.02 to 0.47). These data suggested that NPAHs in the roadway tunnel were directly from vehicle emission while the NPAHs at the roadside were primarily influenced by secondary atmospheric formation

Table 1 Comparison of various NPAH concentrations (pg/m^3) in PM$_{10}$ samples from a roadside site and a roadway tunnel

| Compound | Warm season (roadside) | | | | Cold season (roadside) | | | | Roadway tunnel | |
| | Daytime | | Nighttime | | Daytime | | Nighttime | | | |
	Range	Mean ($n = 25$)	Range	Mean ($n = 25$)	Range	Mean ($n = 25$)	Range	Mean ($n = 25$)	Range	Mean ($n = 6$)
9NA	3.6–50.2	17.5	3.6–199	44.2	15.9–180	64.4	23.8–2319	619	84.6–155	121
2+3NF	22.3–120	49.0	21.8–326	90.7	40.8–654	179	65.3–4714	1012	148–486	264
1NP	5.1–10.2	7.7	5.6–16.0	8.8	7.7–32.9	15.7	6.7–230	41.6	630–1312	985
7NBaA	2.9–10.0	4.2	3.2–50.6	11.1	1.7–11.9	6.6	4.5–231	70.7	41.5–86.9	55.7
6NBaP	3.0–10.7	5.6	2.7–14.9	7.0	4.2–19.7	10.7	5.3–104	27.2	129–230	184
∑NPAHs*	37.9–175	84	39.3–507	161.8	73.5–802	276	109–6195	1770	1210–1931	1610

* ∑NPAHs, the sum of 9NA, 2+3NF, 1NP, 7NBaA and 6NBaP.

(Arey, 1998; Dimashki et al., 2000; Bamford and Baker, 2003; Reisen and Arey, 2005). The value of ∑NPAHs in the cold season was, on average, 2.3 (daytime) and 9.9 (nighttime) times higher than that in the warm season. This could be partly explained by variations of temperature inversion (which are very common in the winter season, trapping pollutants at ground level) (Li et al., 2006); ambient temperature and solar ultraviolet irradiation (both lower in winter and thus causing less photolysis) (Albinet et al., 2008); their precursor PAHs and the atmospheric oxidant NOx (Atkinson and Arey, 1994, 2007; Reisen and Arey, 2005; Wu et al., 2010); and the PM$_{10}$ loading in air (high levels of PM$_{10}$ most frequently occur in winter). Lower temperature generally accompanies temperature inversion and lower solar irradiation. The individual NAPHs were significantly negatively correlated with ambient temperature (T) (Table 2) indicating that temperature was an important factor affecting the accumulation and dilution of NPAHs in PM$_{10}$ at this site. The significant positive correlations between NPAHs and their parent PAHs and NO$_2$ suggested that NPAHs were formed through the nitration of PAHs by NO$_2$ or emitted by similar sources or had similar environmental behavior. Air pollutants, such as SO$_2$, NO$_2$, and ∑PAHs were also found to be significantly negatively correlated with ambient temperature at the $p < 0.01$ level in both daytime and nighttime sampling periods. The strong statistical correlation between temperature and the above air pollutants indicated that temperature was also an important factor resulting in the increased levels of these air pollutants in cold season. The correlations between SO$_2$, NO$_2$, CO, PAHs, PM$_{10}$ and NPAHs in Table 2 probably resulted from the fact that all these air pollutants were influenced by temperature and showed an increase in cold season. In contrast to the increase of NPAHs in the cold season, the concentration of the sum ∑PAHs was, on average, 2.2 (daytime) and 5.3 (nighttime) times higher in the cold season than in the warm season (Wu et al., 2010), indicating that there was more NPAHs formation at nighttime in the cold season than that in the warm season, assuming that NPAHs were synchronously emitted from vehicle engine with PAHs. In addition, for SO$_2$, NO$_2$, CO, O$_3$ and PM$_{10}$ in the cold season, no more than a 50% increase (decrease for O$_3$ and wind speed) was observed for both daytime and nighttime with respect to those in the warm season. Thus, it can be proposed that there was more input of NPAHs in the local atmosphere and temperature inversion had a limited direct

Table 2 Pearson correlations coefficients ($n = 50$) between individual NPAHs with SO$_2$, CO, NO, NO$_2$, O$_3$, PM$_{10}$, PAH concentrations and with temperature and wind speed (WS) at the roadside site

	Time	9NA	2+3NF	1NP	7NBaA	6NBaP
SO$_2$	Day	0.329*	0.457**	0.427**	0.211	0.264
	Night	0.320*	0.299*	0.142	0.301*	0.182
CO	Day	0.454**	0.653**	0.365**	0.243	0.192
	Night	0.398**	0.481**	0.213	0.168	0.086
NO	Day	0.334*	0.694**	0.318*	0.121	0.129
	Night	0.323*	0.064	0.156	0.414**	0.226
NO$_2$	Day	0.584**	0.825**	0.484**	0.346*	0.315*
	Night	0.553**	0.387**	0.361*	0.576**	0.445**
O$_3$	Day	−0.366**	−0.395**	−0.06	−0.188	0.062
	Night	−0.379**	−0.261	−0.347*	−0.478**	−0.362**
PM$_{10}$	Day	0.464**	0.498**	0.380*	0.311*	0.312*
	Night	0.432**	0.437**	0.445**	0.254	0.365*
Temp.	Day	−0.539**	−0.381**	−0.528**	−0.438**	−0.534**
	Night	−0.571**	−0.453**	−0.436**	−0.481**	−0.515**
WS	Day	−0.360*	−0.556**	−0.376**	−0.239	−0.18
	Night	−0.372**	−0.068	−0.037	−0.312*	−0.162
Ant	Day	0.762**	0.676**	0.714**	0.62**	0.635**
	Night	0.507**	0.801**	0.924**	0.699**	0.864**
Flua	Day	0.693**	0.577**	0.744**	0.56**	0.685**
	Night	0.478**	0.8**	0.89**	0.64**	0.829**
Py	Day	0.709**	0.587**	0.709**	0.556**	0.645**
	Night	0.56**	0.788**	0.872**	0.69**	0.85**
BaA	Day	0.76**	0.683**	0.724**	0.574**	0.635**
	Night	0.743**	0.736**	0.86**	0.872**	0.931**
BaP	Day	0.756**	0.696**	0.675**	0.568**	0.588**
	Night	0.748**	0.711**	0.825**	0.871**	0.911**

Ant: anthracene, Flua: fluoranthene, Py: pyrene, BaA: benz[a]anthracene, BaP: benzo[a]pyrene (Wu et al., 2010).
* Correlation significant at $P < 0.05$ level (2 tailed);
** Correlation significant at $P < 0.01$ level (2 tailed).

influence on the enhanced levels of NPAHs in the cold season.

For the semi-volatile PAH and NPAH compounds, the low temperature also favored the particle-phase because the phase distribution depends substantially on vapor pressure, which is temperature-dependent (Albinet et al., 2008). Based on the relationship between the fraction of 3-nitrophenanthrene in the particle phase and the external temperature (Albinet et al., 2008), up to 20% of particle-phase 9NA (with the same molecular weight as 3-nitrophenanthrene) increased in the cold season with respect to that in the warm season at the roadside. But, for the other five NPAHs detected in this study, the gas-phase fractions were negligible because these compounds exist almost entirely in the particle phase in the atmosphere (Albinet et al., 2007). Therefore, the contribution of gas-to-particle partitioning of NPAHs due to the low temperature during the cold season could be neglected assuming there

was no new input of NPAHs. Much higher OH radical reactivity (defined as the reciprocal of the OH radical life time) is reported in winter than in summer due to the high level of pollutants in New York and Santiago de Chile (Ren et al., 2006; Elshorbany et al., 2010). The increased particulate PAHs and NOx in the cold season may have contributed to the increased production of NPAHs due to the increased yield of NO$_3$ radicals in the nighttime and OH radicals in the daytime (Atkinson and Arey, 1994, 2007; Bamford and Baker, 2003; Shao et al., 2004; Reisen and Arey, 2005; Acker et al., 2006; Esteve et al., 2006; Nishion et al., 2008; Ma et al., 2011). As the prevailing wind direction was mostly from the northeast (accounting for more than 80%) during both seasons, the air mass travelling from upwind cities with domestic heating in winter might contribute to the increased PAHs and NPAHs. However, the aging and diagnostic ratios of PAHs nearly coincided with those freshly emitted from vehicles (Wu et al., 2010). Thus, NPAHs which are more easily degraded than their precursor PAHs (Hayakawa et al., 2002) would be expected to be from locally, instead of regionally, formed sources. Based on the analysis above, the enhanced concentrations of NPAHs in PM$_{10}$ in the cold season could be attributed mostly to the increased photochemical formation (increased PAHs and reactive species accompanied by decreased temperature) followed by less photodegradation and temperature inversion at the roadside.

Similar seasonal patterns of NPAHs associated with particulate matter have been reported in other cities and areas such as Shenyang (Tang et al., 2005; Hattori et al., 2007), Mexico (Valle-Hernández et al., 2010), Tokyo (Kakimoto et al., 2000), and an Alpine valley (Albinet et al., 2008) and domestic heating (more emission from coal combustion), low degradation (less loss) and temperature inversion (accumulation) were regarded as the main causes for the enhanced NPAHs in winter. On the contrary, higher levels of 9NA, 2NF and 6NBaP in summer and autumn and the highest levels of 1NP and 7NBaA in spring were

reported in the urban area of Algiers (Ladji et al., 2009). Wilson et al. (1995) also reported higher levels of 9NA and 2NF in summer and autumn and lower levels of 1NP in summer in Houston, Texas. Unlike the previous causes, seasonal changes of ambient temperature as well as the atmospheric reactive species NO$_2$, O$_3$ and OH radicals are attributed to the observed seasonal variations of NPAHs at the roadside in Xiamen. Thus, the seasonal changes of NPAHs in PM$_{10}$ should be evaluated based on ambient temperature as well as local atmospheric oxidants.

Two selected nitro-PAHs, 9NA and 1NP, with certified concentrations in diesel particulate matter (NIST, 2006), were much higher than those measured in Copenhagen and Los Angeles but slightly higher than or comparable to those in Birmingham, Baltimore, Marseilles and Ho Chi Minh City (Table 3). The data in Tables 1 and 3 suggest that the roadside air is heavily contaminated by NPAHs, and the levels will increase with the increasing number of registered vehicles in Xiamen if there are no effective control measures for vehicle exhaust. Understanding the pollution level of NPAHs in PM$_{10}$ is very important to enhance the risk assessment of respirable particles (PM$_{10}$) because certain of these compounds, such as 1-NP and 3-NF, are strong direct mutagens. As shown in Table 3, the average ratios of 9NA to 1NP (9NA/1NP) were also higher than other areas except Baltimore and Los Angeles (afternoon samples), tunnel samples (0.64 in Dimashki et al., 2000; 0.12 this study), and diesel particulate reference materials (0.08–0.8 in Bamford and Baker, 2003), again suggesting the importance of the secondary atmospheric formation of NPAHs and the fast atmospheric transformation of PAHs initiated by OH and/or NO$_3$ radicals at the roadside site.

2.2 Diurnal variation of NPAHs

To better illustrate the diurnal variation of NPAHs, the sampling period was further divided into 10 sub-periods (Fig. 2a). They demonstrated a distinct diurnal variation characterized by high concentration in the nighttime and enhanced day-night difference in the cold season. The
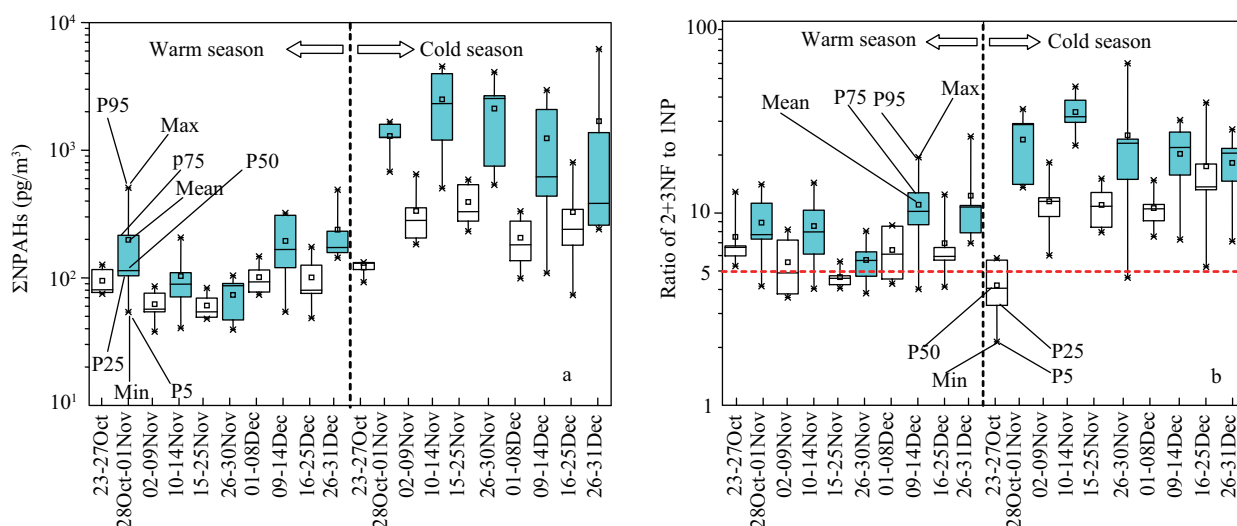
Fig. 2 Diurnal variation of ∑NPAHs (a) and 2+3NF/1NP ratio (b) in the ten sub-periods. The values of the maximum, the 95th, 75th, 50th (median), 25th, and 5th percentile, and the minimum are illustrated by box-whisker symbols and the arithmetic means are presented as "□". Night samples are marked in cyan.

Table 3   Comparison of particle-associated 9NA and 1NP concentrations (pg/m^3) with those reported for other locations

City/Country	Location	Sampling period	9NA	1NP	9NA/1NP	Reference
Birmingham/UK	Urban	1995.11–1996.2	34–520	19–204	1.4	Dimashki et al., 2000
Copenhagen/Denmark	Traffic	1998.1–1999.2	63 ± 30	127 ± 44	0.52	Feilberg et al., 2001
Baltimore/USA*	Urban	2001.1	38–98	14–45	2.4	Bamford and Baker, 2003
Los Angeles/USA	Traffic	2003.1 (morning)	12	38	0.3	Reisen and Arey, 2005
		2003.1 (day)	13	13	1.0	
		2003.1 (afternoon)	44	12	3.7	
		2003.1 (night)	20	21	1.0	
Marseilles/France*	Urban	2004.7	56.6–227.7	14.9–222.1	1.8	Albinet et al., 2007
Ho Chi Minh/Vietnam	Traffic	2005–2006	–	73 ± 40	–	Hien et al., 2007
Xiamen/China	Roadside	Warm season (day)	3.6–50.2	5.1–10.2	2.2	This study
		Warm season (night)	3.6–199	5.6–16.0	4.4	
		Cold season (day)	15.9–180	7.7–32.9	4.2	
		Cold season (night)	23.8–2319	6.7–230	15.7	
	Tunnel	2008.11	84.6–155	630–1312	0.12	

* Data presented here are the total concentrations (filter plus PUF).

diurnal cycle could be driven in part by the more often occurring temperature inversion, less photodegradation, higher concentration of PAHs and NOx, low wind speed and temperature, and more secondary formation at night. For the data in Table 1, the contributions of 1NP and 6NBaP to ∑NPAHs were higher in day samples compared to night samples, probably reflecting more direct emission from motor vehicles (Arey, 1998; NIST, 2006) and/or their relatively stable characteristics under sunlight in comparison with other NPAHs (Stewart et al., 2010). In contrast, 9NA showed significant night predominance probably due to its decreased photo-stability with a perpendicular nitro group (Stewart et al., 2010), and/or more nighttime formation. As for 3-NF, very low concentrations (accounting for less than 5% of 2NF) were reported in ambient and diesel particulate matter (Bamford et al., 2003; Bamford and Baker, 2003; Saldarriaga et al., 2008). However, high levels of 3NF accounting for up to 50% of 2NF were also reported in a city in Denmark (Feilberg et al., 2001). Considering the relatively low proportion of 3NF relative to 2NF, the ratio of 2+3NF to 1NP (2+3NF/1NP) could have represented the ratio of 2NF to 1NP (2NF/1NP) to a large extent as reported in previous studies (Albinet et al., 2007, 2008). The diurnal changes of the 2+3NF/1NP ratios for each sub-period (Fig. 2b) exhibited a similar trend to ∑NPAHs (Fig. 2a). The 2+3NF/1NP ratios were generally higher than the benchmark ratio of 5 (a ratio > 5 indicating secondary formation of NPAHs) and the much higher nighttime ratios, especially in the cold season, can be attributed to nighttime gas-phase reactions of the parent PAHs with the nitrate radical (Ciccioli et al., 1996; Fan et al., 1996a, 1996b; Hien et al., 2007; Albinet et al., 2008). It should be noted that based on the formation mechanism (Arey et al., 1986; Atkinson et al., 1990; Atkinson and Arey, 1994, 1997; Reisen and Arey, 2005) and the much higher yields of the reactions of PAHs with NO$_3$ than OH (Atkinson and Arey, 1994) it would be anticipated that NPAHs yields would increase significantly with the NO$_2$ concentration at night.

To better understand the influence of air pollutants and meteorological factors on the diurnal variation of NPAHs, the dependent t-test for paired samples was carried out using SPSS 10.0 for Windows (SPSS Inc.) to test the null hypothesis that there was no significant difference between the means of day and night concentrations (Table 4). The results showed that the difference between day and night means of ∑NPAHs, O$_3$, wind speed (WS), temperature (T), 2+3NF/1NP and 9NA/1NP was significant in both the warm and cold seasons. No significant difference was found between day and night means of PM$_{10}$ or SO$_2$ in both seasons, suggesting that the two kinds of pollutants were relatively conservative and/or insensitive to the diurnal variation of vehicle exhausts, photochemical reactions, and temperature inversion. The higher concentrations of CO and NO in the daytime in the warm season reflected more vehicle exhaust, when more PAHs and NPAHs were expected to be emitted. Although no significant diurnal differences for ∑PAHs and NO$_2$ were found, ∑NPAHs, 2+3NF/1NP and 9NA/1NP exhibited significant nighttime predominance in the warm season, probably due to the

Table 4   Paired-samples T-test with 95% confidence intervals of the difference test (2-tailed, $t_{0.05[24]} = 2.064$)

D-N Pair[a]	Warm season		Cold season	
	t_s[b]	Significance level (2-tailed)	t_s	Significance level (2-tailed)
∑PAHs[d]	–0.697	0.492	**–3.35**	0.003
∑NPAHs	**–3.328**[c]	0.003	**–4.788**	< 0.001
CO	**2.746**	0.011	0.088	0.93
PM$_{10}$	1.523	0.141	–0.886	0.385
SO$_2$	0.197	0.845	–1.615	0.119
O$_3$	**5.548**	< 0.001	**6.514**	< 0.001
NO	**3.936**	0.001	1.695	0.103
NO$_2$	1.978	0.06	**–12.42**	< 0.001
WS	**3.23**	0.004	**3.281**	0.003
Temp.	**9.19**	< 0.001	**8.138**	< 0.001
2+3NF/1NP	**–3.334**	0.003	**–4.490**	< 0.001
9NA/1NP	**–3.492**	0.002	**–7.221**	< 0.001
BaA/Chr[d]	1.043	0.307	–1.949	0.063
BaP/BeP	**2.242**	0.034	–1.997	0.057

[a] Paired difference of daytime level (D) minus nighttime level (N);
[b] T-test statistics is calculated according to $t_s = \bar{D}\sqrt{n}/$SD, where, $\bar{D}$ is the arithmetic mean of difference between daytime and nighttime, n is the sample number and SD is the standard deviation;
[c] Bold indicates a statistically significant difference (its absolute values is larger than $t_{0.05[24]}$).
[d] Data from Wu et al. (2010).

daytime photodegradative loss of PAHs and more night-time reaction of the nitrate radical with PAHs. In the cold season, the day-night difference became significant for $\sum$PAHs and NO$_2$, but no statistical difference was found for CO and NO. Higher concentrations of both PAHs and NO$_2$ caused by the more often occurring temperature inversion were expected to speed up the nighttime nitration of PAHs. However, the daytime predominance of CO and NO directly emitted from vehicles was suppressed by the temperature inversion at night. O$_3$ reacts with NO to produce NO$_2$, which further reacts with O$_3$ to produce the NO$_3$ radical for the nocturnal periods (NO + O$_3$→ NO$_2$ + O$_2$; NO$_2$ + O$_3$→NO$_3$ + O$_2$) (Wallace and Hobbs, 2006). NO$_3$ can hardly exist during daytime because of its fast photolysis. Moreover, the OH radical concentration showed an increase in the morning and was maximized at midday, mainly dominated by the sunlight, and its concentration was insignificant at night (Kameda et al., 2004). The diurnal variations of OH and NO$_3$ radicals, together with their production yield with PAHs, were expected to influence the diurnal variations of NPAHs to a great extent (Atkinson and Arey, 1994).

A number of studies also show that some NPAHs are readily decomposed when exposed to light, and their half-lives depend strongly on aerosol chemical composition (Fan et al., 1996a, 1996b; Feilberg and Neisen, 2000, 2001). Fan et al. (1996b) find that the half-lives of atmospheric particulate NPAHs from photolysis and from dark heterogeneous reactions with O$_3$ are about 1 and 29 hr, respectively. In contrast, the aging and photo-chemical degradation markers of two PAHs ratios, benzo[a]anthracene/chrysene (BaA/Chr) and benzo[a]pyrene/benzo[e]pyrene (BaP/BeP), do not show significant day-night difference except BaP/BeP in the warm season (Wu et al., 2010). In addition, a "carry-over" from the daytime OH radical-initiated formation of NPAHs would contribute to the nighttime NPAHs. Nonetheless, day "carry-over" contribution was of minor significance to nighttime NPAH because the day-night differences of NPAHs were much greater than those of PAHs. Similarly, the nighttime "carry-over" also contributed to the daytime concentration, but the fact that the daytime low level closely followed the nighttime high level emphasized the influence of the daytime photodegradation and/or vertical dilution on the diurnal variation (Fan et al. 1996a; Feilberg and Neisen, 2000). These results tended to suggest that the diurnal variations of NPAHs were likely influenced, in order of importance, by the diurnal variations of atmospheric oxidants and PAHs, sunlight intensity, thermal inversion and direct emission.

2.3 Airborne exposure to NPAHs in PM$_{10}$

NPAHs are classified into Group 2B (possibly carcino-genic to humans, such as 1NP) and Group 3 (not classifiable as carcinogenic to humans, such as 7NBaA, 6NBaP, and 3NF) (IARC, 1989). Supposing an adult inhales daily about 20 m^3/day of air and spends 12 hr/day and 12 hr/night at the roadside site, his/her average 12 hr (day and night) exposure to six NPAHs in PM$_{10}$ in
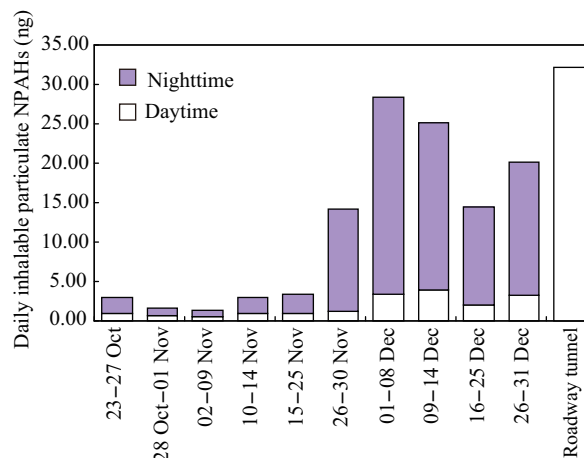

Fig. 3 Daily inhalable exposure to six NPAHs at the roadside in daytime and nighttime and in the roadway tunnel.

each sub-period can be calculated (Fig. 3). The day-night differences in the amount of NPAHs exposure in the cold season were significantly greater than those in the warm season, suggesting that the inhalation risk assessment of exposure to NPAHs in PM$_{10}$ must take into account both seasonal and diurnal variations. The daily inhalable exposure of NPAHs in PM$_{10}$ in the roadway tunnel was much higher than those in the ambient air, suggesting that air pollution in the roadway tunnel was serious due to the weak ventilation and photodegradation. One hour inhalation exposure to the tunnel level was equivalent to around 2-day and 10-hr (daytime) exposure to the ambient level in the warm and cold season, respectively. To date, the total length of roadway tunnels in Xiamen is 74 km and people spend more and more time in the roadway tunnels on the way between home and office. Thus, the potential risk assessment of inhalation exposure to NPAHs in PM$_{10}$ may need to consider the high levels and residence time in the roadway tunnels as well as the seasonal and diurnal variations of these pollutants.

3 Conclusions

In this study, the occurrence of six NPAHs in PM$_{10}$ from a roadside site and roadway tunnel were measured. The difference of the relative distribution between ambient and tunnel samples suggested that the source of NPAHs at the roadside was mainly secondary atmospheric formation. Significant seasonal and diurnal variations of NPAHs in PM$_{10}$ were observed, and the diurnal variation of NPAHs in PM$_{10}$ collected in the cold season was more significant than that in the warm season. The seasonal variations could be mainly driven by secondary atmospheric formation, thermal inversions, and photochemical degradation; while the diurnal variations could be attributed to the diurnal variation of precursor PAHs and atmospheric oxidants, sunlight and temperature inversion. Decreased temperature in winter results in more accumulation of reactants such as PAHs, NO$_2$ and other atmospheric oxidants in the air, and more reactants lead to more nitro derivatives of PAHs. It is just like a domino effect. Although one roadside sampling site cannot give an overall picture of the occurrence of

NPAHs in PM_{10} in the city of Xiamen, the results gathered here may throw light on the investigation of secondary organic pollutants in PM_{10} in other busy traffic areas. The ambient temperature should be considered as an important factor in the health risk assessment of NPAHs in PM_{10}. Moreover, more attention should be paid to roadway tunnel air pollution based on the fact that most cities are seeing rapid urbanization in China, and a resultant increase in road tunnels. In the future, more intensive sampling procedures (4 hr interval over 24 hr) including measurement of gas- and particle-phase NPAHs, NO_3 and OH radical at roadside, urban and rural background sites are required in order to investigate the mechanism(s) controlling their diurnal and seasonal variations.

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