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Acyl peroxy nitrate measurements during the photochemical smog season in Beijing, China

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Abstract

In situ measurements of acyl peroxy nitrates (PANs), including peroxyacetyl nitrate (PAN), peroxypropionyl nitrate (PPN), and peroxymethacryloyl nitrate (MPAN), were conducted using a gas chromatography-electron capture detector (GC-ECD) system during the photochemical smog season in Beijing, China. The maximum mixing ratios were 17.81, 2.48, and 0.27 ppbv for PAN, PPN, and MPAN, respectively. During the measurement period, PAN levels twice exceeded the maximum recommended mixing ratio established by the World Health Organization (WHO). Average ratios of PAN/PPN, PAN/MPAN, and PPN/MPAN were 7.41, 47.65, and 6.91, respectively. The average ratio of PAN/O_3 (0.15) in Beijing was significantly higher than those in other areas studied. The frequencies of PANs showed both Gaussian and Weibull modes of distribution. Wind direction was closely related to PAN variation. Anthropogenic sources played an important role in PAN formation, as estimated from PPN and MPAN levels. Relative humidity (RH) and total particle surface area were related with the heterogeneous reactions of PANs with surface concentrations of particulate matter ≤10 µm in diameter.

1 Introduction

Acyl peroxy nitrates (PANs), including peroxyacetyl nitrate (PAN), peroxypropionyl nitrate (PPN), and peroxymethacryloyl nitrate (MPAN), play important roles both in atmospheric chemistry and in human health. PAN provides a better indicator of photochemical smog than does O_3, due to its negligible natural background levels. One notable feature of PAN is that, its depletion time by new NO emissions is associated with its cleavage, and can be considerably longer than that of O_3 (Rappenglück et al., 2003; Bottenheim et al., 1994). PAN is also an excellent indicator of poor air quality, as its only source in the atmosphere is tropospheric photochemistry (Carter et al., 1981; Schrimpf et al., 1995). Some O_3 is of stratospheric origin and is transported to the

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surface of the earth without any accompanying PAN (McFadyen and Cape, 2005). Previous studies have indicated that PAN has lachrymatory (Altshuller, 1978), phytotoxic (Taylor, 1969; Sun and Huang, 1995), and mutagenic effects (Shepson et al., 1986). Furthermore, PAN and some of its analogs have been found to be 10–50 times more toxic to plants than O_3 (Taylor, 1969; Gaffney and Marley, 2001a, b). Singh (1987) first reported that PAN could act as a means of transporting NO_2 over very long distances. Therefore, it is a globally important chemical, rather than just an urban air pollutant. Other studies have also indicated that high PAN concentrations in suburban and rural areas showed the greatest effects on local air quality (Tsalkani et al., 1991; McFayden and Cape, 1999). PPN is also a medium for storing NO_2 and leads to the formation of PAN (Gaffney and Marley, 2001b). PPN is four times more phytotoxic than PAN (Kleindienst et al., 1990) and has an eye-irritant effect five times greater than that of PAN (Altshuller, 1978).

Previous studies have confirmed that PAN is more mutagenic than PPN (Kleindienst et al., 1990). Like O_3, PAN and associated organic nitrates are greenhouse gases (Gaffney and Marley, 1991). To date, there have been fewer studies of PPN (Grosjean, 2003) than of PAN. Historically, a few publications have examined PAN or PPN in East Asia (Chang and Tso, 1994; Zhang and Tang, 1994; Sun and Huang, 1995; Lee et al., 2008); however, studies of PANs in urban areas of China were limited. Conversely, extensive studies of PANs have been implemented in North America (Singh and Salas, 1989; Williams and Grosjean, 1991; Shepson et al., 1992; Roberts et al., 2007; William et al., 1993; Williams et al., 1997; Nouaime et al., 1998; Roberts et al., 1998), particularly in southern California, where PAN was first found in the 1960s (Grosjean, 2003). There have also been some field studies of PANs in Europe (Solberg et al., 1997; Hansel and Wisthaler, 2000; Whalley et al., 2004).

Photochemical air pollution is a major problem in Beijing, China (Guttikunda et al., 2001; Ding et al., 2008). O_3 and NO_x episodes have been studied extensively in this region (Xu et al., 2008; Duan et al., 2008; An et al., 2007), however, there have been comparatively few studies on PANs. With such limited information available on PANs

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despite the rapid development and urbanization of Beijing, particularly the increase in traffic density (Zhao, 2005), it is necessary to obtain a deeper understanding of PANs in Beijing.

In this study, PANs were sampled and analyzed in Beijing, China and preliminary comparisons with other cities or regions were made. The relationships among PAN, PPN, MPAN, and O_3 were discussed, estimations of the levels and roles of anthropogenic hydrocarbons (AHCs) and biological hydrocarbons (BHCs) in PAN formation by PPN and MPAN were made, and potential meteorological impacts on PANs and their possible heterogeneous reactions were studied.

2 Experimental methods

PANs, including PAN, PPN and MPN, were measured continuously on the campus of Peking University (PKU Site), Beijing (Fig. 1) as part of the CAREBEIJING 2007 campaign. Peking University is located in an urban area with high population density and heavy traffic. The sampling site was on the roof of the six-story PKU Scientific Building (39°59′20.92″ N, 116°18′25.91″ E), west of Zhongguancun Street, at a height of 25 m.

Ambient PANs were measured using a gas chromatography-electron capture detector (GC-ECD) system. Detailed information about this instrument is available in Williams et al. (2000). The column (model DB-210, 0.53-mm internal diameter (ID); J&W Scientific, Folsom, CA) was wrapped around an aluminum block, which was thermoelectrically cooled to 15 °C to minimize the thermal decomposition of PANs. During sample loading, the oven was also cooled to 15 °C. Helium and nitrogen were separately used as the carrier and make-up gas at 15 standard cubic centimeters per minute (sccm) and 30 sccm, respectively. Whole-air injection pipes were made from a 2-mL sample loop composed of a perfluoroalkoxy (PFA) pipe with an outside diameter (OD) of 1/8 inch. Ambient air at 1 standard liter per minute (slpm) was drawn automatically through a Teflon sampler at 5-min intervals using a Teflon six-port rotary valve (VICI Valco Instruments Co., Inc., Houston, TX) and a diaphragm pump. The ECD was the

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Shimadzu GC Mini-2 ^{63}Ni model and was maintained at 40 °C during instrument operation. The detection limits for PAN, PPN, and MPAN were 5, 10, and 15 parts per trillion by volume (pptv) with an uncertainty of 2σ.

All inlets were made of Teflon to minimize the loss of PANs inside them and to prevent the heterogeneous formation of PANs. Standard PAN gas was prepared directly through the reaction of CH_3COCH_3 with NO under ultraviolet (UV) light at a wavelength of 285 nm. The purity of PAN was higher than 99.7%. Liquid phase PPN was synthesized in the laboratory and then volatilized for calibration. The response ratios to the ECD of PPN and MPAN were 0.84 and 0.72, respectively, as compared to the reference value of PAN response to the ECD. These response factors were determined in the laboratory through simultaneous measurements of each compound using a high-sensitivity NO_y ambient air analyzer and the GC-ECD. Calibration was performed before and after the measurement period, and there were no significant changes during the measurement period.

O_3 was measured using an EC9810 ozone analyzer (ECOTECH Co., Hong Kong, China) with a detection limit of 1 part per billion by volume (ppbv). NO_x were measured using a high sensitivity NO_x analyzer (ECOTECH) with a detection limit of 0.4 ppbv. Both instruments were dynamically calibrated using a dynamic dilution calibrator (ECOTECH). Since chemiluminescent based NO_x analyzer measured NO_x was the sum of NO_2, NO, and PANs, the actual NO_2 mixing ratio was estimated by subtracting the levels of NO and PANs from the NO_x level. A twin differential mobility particle sizer combined with an aerodynamic particle sizer (TSI model 3320, TSI Co., Shoreview, MN) was used to measure particle size distributions (particle diameters ranged from 3 nm to 10 µm). Details of the equipment used have been described previously (Liu et al., 2008).

All of the examined pollutants and corresponding meteorological parameters (including temperature, relative humidity (RH), atmospheric pressure, wind speed, wind direction, levels of UV-A and UV-B light, and precipitation) were continuously measured from 14 to 19 August 2007.

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Table 1 indicates a data-capture rate of almost 100% for PAN and PPN; that for MPAN was somewhat lower (77.5%), because the level of ambient MPAN was lower than the levels of ambient PAN and PPN. Moreover, , the reduced sensitivity of the instrument to MPAN also resulted in lower data reporting in comparison with that for PAN and PPN. Data recovery rates for all three molecules ranged from 99.5% to 99.7%, which was sufficient for further studies.

3 Results

3.1 Field measurements

During the CAREBEIJING 2007 campaign, the average temperature was 29.4 °C (23.4–37.3 °C), the average RH was 56.7% (22.2–84.8%), and UV-B averaged 0.15 W m^{-2} (0.01–0.66 W m^{-2}) (Fig. 2). There was little precipitation, except on 16 August, when 0.2–15.4 mm of precipitation occurred between 07:10 and 07:20, at 08:00, at 12:30, and between 18:00 and 18:40. As the precipitation intensity was quite low and the regional weather system remained mild, no significant UV or temperature fluctuations appeared before or after the precipitation (Fig. 2).

A weak pressure system (994.3–1004.1 hPa; Std. dev. = 2.47) led to stagnant atmospheric conditions. Wind speed ranged from 0 to 3.98 m s^{-1} (Fig. 3), with 81% of the measurement data (n = 862) showing <2 m s^{-1}. The frequency of stagnant conditions (wind speed <0.3 m s^{-1}) was low (16.1%). Wind became slightly stronger in the afternoon (12:00–18:00 h, local time). The prevailing wind direction was almost constant during the measurement period, from north to south (Fig. 2). At about 06:00 h, the wind direction was primarily from the northwest, with northerly winds prevalent during the night. In addition, the boundary layer was generally below 1 km, which promoted PANs and ozone accumulation.

As shown in the time series in Fig. 2, PAN pollution levels were highest, followed by PPN and MPAN. PANs maintained high mixing ratios, with averages of 3.79, 0.56,

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and 0.09 ppbv for PAN, PPN, and MPAN, respectively. On 15 August, PANs reached their maxima of 17.81, 2.48, and 0.27 ppbv, respectively. Daily maximum levels of PANs generally occurred at about 12:00 h local time, earlier than those of O_3 (Fig. 2). Related studies have indicated that O_3 levels increase with increasing temperature (Wunderli and Gehrig, 1991; Sillman and Samson, 1995). One reason for this observed difference was the instability of PAN (Sillman and Samson, 1995). The daytime peak always occurred between 16:00 and 18:00 h. The pollution level of MPAN was similar to that recorded in Nashville, Tennessee, in the United States (Roberts et al., 1998). As the mixing ratio of ambient MPAN was much lower than those of PAN and PPN (Roberts et al., 1998, 2002, 2007), the detection limit of MPAN for the GC-ECD instrument used in this study was only 15 pptv; therefore, more significant fluctuations could be seen for MPAN levels, as shown by its time series (Fig. 2). The sub-peaks of PAN and PPN were easy to identify. However, for MPAN, sub-peak detection was much more difficult. Further studies will require an instrument with a higher sensitivity and lower detection limit for MPAN.

Table 2 summarizes the maxima, minima, averages, standard deviations (SD), and median values for PAN, PPN, MPAN, and O_3. As shown in Table 2, the ratios of the minima to maxima were low and the SD values were high, indicating high dispersion among mixing ratios during the measurement period. For the characterization of photochemical pollution in Beijing, the mixing ratios of PANs were classified by daytime and nighttime in Table 2. The daytime maxima of PAN, PPN, and MPAN were consistent with their corresponding daily maxima. The daytime minimum of PAN was higher than its daily minimum. For PAN, the daytime maximum, minimum, and average were higher than those at night. For PPN and MPAN, the daytime maxima and averages were also higher than those at night, although the minima were essentially the same. The nighttime PAN maximum was occasionally higher than 5 ppbv, and the nighttime minimum may have exceeded that of O_3.

PAN is highly phytotoxic and can damage vegetation at concentrations as low as 5 ppbv (Sun and Huang, 1995; Cape, 2003). Concerned by the health effects of PAN

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episodes, and to prevent vegetation damage, the World Health Organization (WHO) set an air quality guideline of 5 ppbv over 8 h for PAN (WHO, 1987). PAN levels exceeded this threshold twice during the present measurement period, on 15 August from 10:40 h to 19:10 h and on 17 August from 10:10 h to 18:30 h. Maximum concentrations reported for Swiss sites were <5 ppbv (Wunderli and Gehrig, 1991). In the United Kingdom, concentrations of 0.5 ppbv were typical in the summer and levels were highest during photochemical episodes. During such periods, PAN concentrations were typically 1% of those of ozone (Photochemical Oxidant Review Group, 1993). In this study, the maximum ratio of PAN to O_3 reached 15%, much higher than 1%.

High PAN levels have been detected in other large metropolitan areas. PAN values of up to 12 ppb have been reported in Athens, Greece (Suppan et al., 1998), and in Santiago, Chile, PAN levels >20 ppb were measured (Rappenglück et al., 2000). Therefore, it is imperative that this serious pollution problem be resolved in Beijing, although the O_3 mixing ratio was not excessive during PAN episodes. A comprehensive comparison of the concentrations of PANs in Beijing with those in other regions is summarized in Table 3. PAN levels as high as 80 ppbv (about 400 mg m^{-3}) have been detected under inversion conditions in California's south coast basin (Tuazon et al., 1981). High levels of PAN pollution, especially PAN and PPN, were reported in 1997 in Mexico City, with a maximum of 34 ppbv and a daily average maximum of 15 ppbv (Gaffney et al., 1999). However, a later study indicated that PAN pollution was decreasing in Mexico City, with an average daily maximum in 2003 of 3 ppbv (Marley et al., 2007). PAN concentrations were found to be important for the correct prediction of photochemical O_3 production rates, as they have a large influence on local concentrations of peroxyl radicals (Ridley et al., 1999). The high levels of PAN pollution undoubtedly contributed to O_3 production rates in these other areas. PAN, as a reservoir of NO_x, can contribute to a significant amount of surface ozone through thermal decomposition (Marcelo et al., 2007).

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3.2 Diurnal variations and frequency modes

Diurnal variations of PANs and O_3 are shown in Fig. 4. PANs exhibited typical diurnal variations driven by sunlight, with daily peaks occurring at noon or in the afternoon. Additional sub-peaks were also observed during rush hours, but these values were much lower than the daily maximum. Also, as shown in Fig. 4, diurnal variations in O_3 were similar to those of PANs, although the O_3 peak occurred later than that of PANs. The diurnal profiles were similar to those recorded at other locations (Sun and Huang, 1995; Grosjean et al., 1996). There are at least two possible explanations for why high PAN pollution levels contributed to a broader peak of O_3 on the following day: first is the high concentration of PANs in comparison to NO_x (Table 4); second, the thermal loss of PANs, especially PAN, could lead to a significant contribution of NO_2 to NO_x through photolysis during the following morning (Fig. 4). The frequencies of PANs (as shown in Fig. 5) showed both Gaussian and Weibull modes of distribution.

A strong correlation was observed between PAN and PPN during the measurement period (Fig. 6, $R^2 = 0.96$). Previous studies by Grosjean et al. (1996) and Roberts et al. (1998, 2002) found that the ratio of PAN to PPN was below 7.4 in Los Angeles, indicating that this area was dominated by anthropogenic hydrocarbons (AHCs). In this study, the ratio was 6.6 ($n = 864$), and therefore it was concluded that photochemical pollution in Beijing is mainly due to AHC pollution. The ratio of PAN to PPN was a better photochemical indicator than ozone (or PAN) alone. Singh and Hanst (1981) reported a PAN: PPN ratio of 6.13–6.90 in Los Angeles from 9 to 21 April 1979, and Grosjean et al. (1996) reported a ratio of 7.35 in Los Angeles from 29 August to 13 September 1993.

Similar to other air pollutants, the absolute mixing ratios of PANs were strongly controlled by dispersion. However, relative mixing ratios were less affected. Thus, sources and sinks mainly determine the values of ratios. As these sources and sinks are broadly similar among urban sites in industrialized nations, these ratios will be less variable. PAN/PPN ambient concentration ratios reflect differences in formation and removal rates. In a detailed examination of emission inventory data for hydrocarbons

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that are precursors to PAN and PPN, the averages (ranges) of all measurements for PAN/PPN, PAN/O_3, PPN/O_3, MPAN/O_3, and PANs/NO_x (Table 4) were as follows: 7.41 (3.00–16.17), 0.23 (0.03–8.07), 0.035 (0.002–1.306), 0.006 (0.001–0.277), and 0.46 (0.012–7.548), respectively.

Typical PAN/PPN ratios are 2.5–10 in urban areas and 3.3–20 in rural areas (Roberts, 1990). PPN production may be more efficient in highly polluted air, presumably due to the higher concentrations of the more reactive PPN precursors typically found in urban areas (Singh and Salas, 1989). However, the shorter processing time for OH reactions with the more reactive PPN also contributes to this effect. Roberts et al. (2002) reported PAN/MPAN ratios as low as 4 near Nashville, TN, during periods with high biogenic hydrocarbon (BHC) levels – a value lower than that (14.92) obtained in the present study. Higher PAN/PPN and lower PAN/MPAN ratios are typical in areas where anthropogenic precursors can dominate PAN production (Roberts, 1990; Altshuller, 1993; Williams et al., 1997; Roberts et al., 2002).

Mixing ratios similar to the PAN/PPN have been reported in studies of other urban areas, indicating similar sources and sinks in all urban environments. In Munich, Germany, the reported ratio was 14.29 (Kourtidis et al., 1993), those in urban areas in the USA were 7.69–33.33 (Singh and Salas, 1989), and ratios of 10–16.67 were reported in Toronto, Canada (Shepson et al., 1992). A somewhat higher ratio of 3.57–7.14 was reported from a site downwind of a mountainous area near Los Angeles (Grosjean et al., 1993). A similar urban PAN/PPN ratio of 8.3 was reported over the upper Rhine Valley in Germany, an area affected by urban emissions (Schmidt et al., 1998).

3.3 Contributions of hydrocarbons to PAN formation, estimated from PPN and MPAN levels

The contributions of AHCs and BHCs to PAN formation were estimated from measurements of PPN and MPAN levels. With regard to volatile organic compounds (VOCs), PAN was formed from both AHC and BHC. PPN was formed mainly from AHC, and 3-hexenal may be a VOC precursor of PPN (Grosjean et al., 1993). Isoprene reacts with

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OH and O_3 to produce methacrolein (MACR) (Tuazon and Atkinson, 1990a), which in turn reacts with OH in the presence of NO_x to produce MPAN (Tuazon and Atkinson, 1990b). MPAN is thus mainly derived from BHC.

On the basis of the discussion in Sect. 3.2.2 regarding the correlations of PAN with PPN, PPN with MPAN, and PAN with MPAN, daily correlation coefficients are plotted in Fig. 7. During the measurement period, the daily correlation coefficients of PAN with PPN were all above 0.8, and PPN with MPAN, and PAN with MPAN showed similar fluctuations, dropping below 0.5 only on 19 August. As shown in Fig. 6, PAN and PPN were strongly correlated ($R^2 = 0.9568$). Thus, PAN and PPN have very similar VOC precursors, and AHCs play an important role in PPN formation. PPN was a tracer for anthropogenic pollution. Therefore, the formation of PAN might be also significantly contributed by AHCs. Regressive fitting was performed on PPN and MPAN data with data for PAN, according to the following equation ($R^2 = 0.97$, $n = 612$) : [PAN] = 5.75 (±0.07) [PPN] +13.08 (±0.81) [MPAN] – 0.06. This R^2 value was higher than that for the correlation between PPN and PAN, further demonstrating the applicability of the mixing ratio of PPN and MPAN to fit that of PAN and providing a rationale for PAN chemistry being based on PPN and MPAN. There has been some reported linearity between PAN and ozone; however, due to their different formation and loss mechanisms, especially for the primary source of ozone, this correlation may be not entirely meaningful. That is, strong correlation coefficients based on these data may be the result of coincidence or simple mechanisms; most such correlations are generated from secondary reactions. In our study, the coefficients were not highly significant.

The correlation of $[PAN]_{measured}$ with $[PAN]_{calculated}$ is shown in Fig. 8. The intercept of 0.15 ppbv can be considered to represent the regional mixing background. Based on Eqs. (1) and (2) below, levels of the sources of PAN from AHC and BHC were calculated and plotted as shown in Fig. 9. Using Eqs. (3) and (4) to calculate the percentages of $[PAN]_{AHC}$ and $[PAN]_{BHC}$, the ratio of $[PAN]_{AHCs}/[PAN]_{BHC}$ is shown in Fig. 9. Equations (1)–(4) are as follows:

$$[PAN]_{AHCs} = [PAN](4.9[PPN]/4.9[PPN] + 8.4[MPAN]), \quad (1)$$

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$$[\mathrm{PAN}]_{\mathrm{BHCs}} = [\mathrm{PAN}](8.4[\mathrm{MPAN}]/4.9[\mathrm{PPN}] + 8.4[\mathrm{MPAN}]), \quad (2)$$

$$[\mathrm{PAN}]_{\mathrm{AHCs}}\% = [\mathrm{PAN}]_{\mathrm{AHCs}} \times 100/([\mathrm{PAN}]_{\mathrm{measured}} - [\mathrm{PAN}]_{\mathrm{background}}), \quad (3)$$

$$\text{and}[\mathrm{PAN}]_{\mathrm{BHCs}}\% = [\mathrm{PAN}]_{\mathrm{BHCs}} \times 100/([\mathrm{PAN}]_{\mathrm{measured}} - [\mathrm{PAN}]_{\mathrm{background}}). \quad (4)$$

In the time series as shown in Fig. 9, $[\mathrm{PAN}]_{\mathrm{AHC}}$ and $[\mathrm{PAN}]_{\mathrm{BHC}}$ maintained good correlation with PAN (Fig. 1). $[\mathrm{PAN}]_{\mathrm{AHC}}$ was generally higher than $[\mathrm{PAN}]_{\mathrm{BHC}}$. On the basis of their ratios (Fig. 9), this trend was significant, with values ranging from 0.62 to 12.05 and exceeding 1 on most occasions (98%, $n = 613$).

3.4 Meteorological impacts on variation in levels of PANs

Wind roses for PANs (Fig. 10a, b, and c) indicate that the mixing ratios of PANs were also governed by meteorological parameters, typically wind direction. Morning and evening peak phenomena of PANs occurred (Fig. 2). In addition, two representative cases, the morning peak on 18 August and the evening peak on 19 August, were studied in detail (Fig. 11). Wind speed, ratio of NO to NO_2, temperature, and O_3 are also plotted on the graphs.

On the morning of 18 August, the levels of PANs began to increase (as indicated by the red arrow in Fig. 11a) at 01:00 h (local time), reached a peak at about 03:00 h, and then decreased. O_3 levels showed a similar trend. The wind was stationary from 02:00 to 03:00 h, and the NO/NO_2 ratio showed no remarkable changes, but the temperature dropped at 01:00 h (black arrow). Factors influencing the formation of PANs include sunlight, VOC precursors, OH radicals, O_2, and O_3. In addition, the loss of PANs is directly dependent on temperature and the NO/NO_2 ratio. The decreasing temperature and almost constant NO to NO_2 ratio led to reduced thermal loss of PANs in the early morning. The small photolytic constant of PANs at ground level, relatively low reactivity with hydroxyl radicals, and water solubility contribute to their stability, particularly at low temperatures. Conversely, at temperatures higher than approximately 20 °C, PANs decompose readily, with complex kinetics, at a rate which is mainly determined by the

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NO/NO_2 ratio. In addition, the lack of wind led to pollutant accumulation, and therefore to the occurrence of early morning peaks in the concentrations of PANs. Interestingly, the peak for PAN was higher than those for PPN and MPAN, perhaps because of differences in their sensitivities to temperature. After 03:00 h, the wind speed increased, which helped to disperse pollutants, and therefore levels of PANs tended to decline. On the night of 19 August, a clear increase in PANs was observed (as indicated by the red arrow in Fig. 11b). From 18:00 h until 20:00 h (local time), O_3 levels did not undergo any remarkable changes. During this period, the temperature and the ratio of NO to NO_2 decreased, and there were no clear changes in wind direction. The loss of PANs is highly dependent on temperature and the ratio of NO to NO_2. High temperatures are associated with greater thermal loss of PANs, whereas high NO/NO_2 ratios are associated with an increase in the loss of PANs.

3.5 Potential formation of PANs through heterogeneous reactions

PANs are known to be quite sensitive to the presence of walls in laboratory studies. Therefore, they likely react with aerosol surfaces. PANs are very soluble in nonpolar organic solvents and may undergo important oxidation reactions on the surfaces of soot particles, leading to the formation of oxidized and nitrated polynuclear aromatic hydrocarbons (Finlayson-Pitts and Pitts, 2000).

During the measurement period, levels of particulate matter ≤2.5 µm in diameter ($PM_{2.5}$) ranged from 1.1 to 286.8 µg m^{-3} (average, 82.0 µg m^{-3}), an appropriate range for heterogeneous reactions. Figure 12 shows the distributions of $PM_{2.5}$ concentrations by number and PM_{10} by surface (PMS). In Fig. 12a, a clear double peak can be seen in the distributions of $PM_{2.5}$ by number, with the centers located around 50 nm and 140 nm, and the 30% value exceeding 100 µg m^{-3}. In Fig. 12b, a trimodal distribution can be seen for PMS. Figure 13 shows the different relationships between PAN (and PPN and MPAN) and PMS. A laboratory study (Langer et al., 1992) indicated that heterogeneous reactions also play an important role in PAN formation, and that PAN is positively related with PMS (Finlayson-Pitts and Pitts, 2000). In this study, no significant

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correlation was observed between PANs and PMS (Fig. 13). High PAN mixing ratios (>5 ppbv) were associated with a PMS of 4–9 × 10^{12} nm^2 m^{-3}. Greater PMS did not lead to higher mixing ratios for PANs. As mentioned in the previous section, PAN and PPN showed a strong correlation (R^2 = 0.95), resulting in similar relationship curves of PMS/RH with PPN and PAN; therefore, the relation of PPN with (PMS/RH) is not shown in Fig. 13.

Relative humidity, which varied widely (22.2–84.8%, SD = 15.3), may affect heterogeneous reactions of PANs. As shown in Fig. 14, RH and total particle surface were related with PAN and MPAN mixing ratios. Because PPN and PAN were strongly correlated, their relations with RH and PMS were very similar. Therefore, PPN results are not shown. High mixing ratios occurred at moderate-to-low RH (35–40% of PAN mixed and ~25% of MPAN mixed) and high PMS values occurred at intermediate RH (PAN, 5–8 × 10^{12} nm^2 m^{-3}; MPAN, 6–8 × 10^{12} nm^2 m^{-3}). Further laboratory experimentation is recommended to clarify whether heterogeneous reactions lead to the loss or formation of PAN.

4 Conclusions

In situ measurements of PAN, PPN, and MPAN revealed episodic high levels of PANs during the photochemical smog season in Beijing, China. Unusual mixing ratios indicated maximum values of 17.81, 2.48, and 0.27 ppbv for PAN, PPN, and MPAN, respectively. PAN levels twice exceeded the maximum recommended mixing ratio established by the World Health Organization (WHO), and therefore represent a serious health risk. The average ratios of PAN/PPN, PAN/MPAN, and PPN/MPAN were also higher than those measured in other areas, especially the ratio of PAN/O_3. The frequencies of PANs basically have two modes. Wind direction is closely related to variations in levels of PANs. Anthropogenic sources play an important role in PAN formation, as estimated from PPN and MPAN measurements. H heterogeneous reactions of PANs related to RH and surface concentrations of PM_{10}.

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Table 1. Data collection efficiencies for PANs.

Species	No. of records		Percent (%)	No. of valid records	Recovery (%)	No.	
	Total	Expected				invalid records	missing records
PAN			98.0	843	99.5	4	17
PPN	791	864	91.6	789	99.7	2	73
MPAN	670	864	77.5	667	99.6	3	194

Notes: Percentages were calculated from the actual obtained number of records divided by the total expected number of records. Percentage recovery was calculated by dividing the obtained number of valid records by the total number of records.

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Table 2. Statistical data for PANs and O_3.

	Value	PAN (ppbv)	PPN (ppbv)	MPAN (ppbv)	O_3 (ppbv)
Total	Max	17.81	2.48	0.27	118.9
	Min	0.31	0.07	0.02	0.2
	Avg	3.79	0.56	0.09	34.5
	SD	3.26	0.50	0.04	29.0
	Median	2.53	0.36	0.08	29.6
Day	Max	17.81	2.48	0.27	118.9
	Min	0.51	0.08	0.02	0.7
	Avg	5.46	0.80	0.11	49.0
	SD	3.82	0.57	0.05	30.1
	Median	4.34	0.64	0.11	50.2
Night	Max	5.78	0.71	0.15	68.0
	Min	0.31	0.07	0.03	0.2
	Avg	2.07	0.29	0.07	19.1
	SD	0.81	0.13	0.03	17.5
	Median	2.04	0.26	0.07	10.9

Notes: Max and min denote maximum and minimum, respectively. Avg indicates geometric average, and SD denotes standard deviation. Day and night indicate time ranges of 07:00–19:00 h and 19:00–07:00 h (next day), respectively.

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Table 3. Regional and worldwide concentrations of PANs, taken from the literature.

Site	Type	Sampling dates	PAN (ppbv) (max, avg)	PPN (ppbv) (max, avg)	MPAN (ppbv) (max, avg)	Reference
Beijing, China	Urban	14–19 August 2007	17.81, 3.79	2.48, 0.56	0.27, <0.015	This study
	Urban	Several days in May and June 1990	6.8, –	–	–	Zhang and Tang (1994)
Seoul metropolitan area, Korea	Urban	May–July 2004 and 2005	10.4, 0.8	–	–	Lee et al. (2008)
Taipei, China	Urban	July 1992–April 1993	27, –	–	–	Sun and Huang (1995)
La Vergne, TN, USA	Suburban	June–July 1995	2.14, 0.48	0.32, 0.005	0.15, 0.03	Nouaime et al. (1998)
La Porte airport, Houston, TX, USA	Suburban	August–September 2000	6.5, –	–	–	Roberts et al. (2003)
Houston metropolitan area, TX, USA	Urban	2000	14, –	–	–	Roberts et al. (2002)
Cornelia Fort Air Park, Nashville, TN, USA	Suburban	14 June–14 July 2000	2.51, 0.674	0.43, <0.005	0.33, <0.005	
Charleston, SC, USA	Marine	12 July–10 August 2002	2.79, 0.36	0.387, <0.004	0.371, <0.004	Roberts et al. (2007)
Athens, Greece	Urban	2001	6.6, –	–	–	Glavas and Moschonas (2001)
Chebogue Point, Nova Scotia, Canada (North Atlantic)	Background	August–September 1993	0.325, 0.049	0.089, 0.009	–	Roberts et al. (1998)
		September 2002	3.9, 2.8	–	–	
		October 2002	3.8, 1.8	–	–	
Santiago, Chile	Urban	December 2002	9.8, 5.3	–	–	Rubio et al. (2004)
		January 2003	22, 6.4	–	–	
		No data	50, –	~6, –	–	Darley et al. (1963)
		1 August–31 December 1967	58, –	–	–	Taylor (1969)
Riverside, CA, USA	Urban	August 1968	28, 5.9	–	–	
		August 1976	20, 3.0	–	–	
		August 1980	22, 5.6	–	–	Temple and Taylor (1983)
Los Angeles, CA, USA	Urban	9–21 April 1979	2.7, 0.72	–	–	Singh et al. (1981)
Porto Alegre, Brazil	Urban	May 1996–March 1997	6.67, –	–	–	Grosjean et al. (2002)
Mexico City, Mexico	Urban	February–March 1997	34, –	–	–	Gaffney et al. (1999)
Azusa, CA, USA	Urban	28 August–11 September 1993	–	1.46, 0.47	–	Grosjean et al. (1996, 2001);
		1 July–16 October 1997	4.8, 0.880	0.72, 0.25	–	Grosjean and Grosjean (1999)
Simi Valley, CA, USA	Urban	18 July–16 October 1997	3.0, 0.608	0.28, 0.13	–	

Notes: Max denotes maximum. Avg indicates average.

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Table 4. Pollutant ratio statistics.

	Value	PAN/PPN	PAN/MPAN	PPN/MPAN	PAN/O_3	PPN/O_3	MPAN/O_3	PANs/NO_x
Day	Max	16.17	166.67	27.47	0.94	0.236	0.024	7.548
	Min	3.56	16.30	1.78	0.03	0.002	0.001	0.019
	Aver.	7.38	58.57	8.58	0.15	0.023	0.003	0.703
	SD	1.71	26.13	4.53	0.11	0.021	0.002	0.983
	Median	6.91	54.66	8.26	0.12	0.017	0.002	0.295
Night	Max	14.31	91.36	14.86	8.07	1.306	0.277	1.003
	Min	3.00	14.92	1.19	0.04	0.003	0.001	0.012
	Aver.	7.46	35.71	4.98	0.31	0.050	0.010	0.178
	SD	1.82	12.47	2.14	0.52	0.085	0.020	0.170
	Median	7.46	33.31	4.68	0.19	0.029	0.004	0.119

Notes: The definitions of day and night follow those in Table 2. Max, min, avg and SD denote maximum, minimum, average, and standard deviation, respectively.

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Fig. 1. Location of measurement site during the CAREBEIJING 2007 campaign. Circle indicates the sampling site on the roof of the Scientific Building of Peking University (PKU), the highest building in the immediate vicinity. Zhongguancun Street locates in east of the sampling site. The PKU gymnasium, the site of the 2008 Olympics ping pong competition, is nearby.

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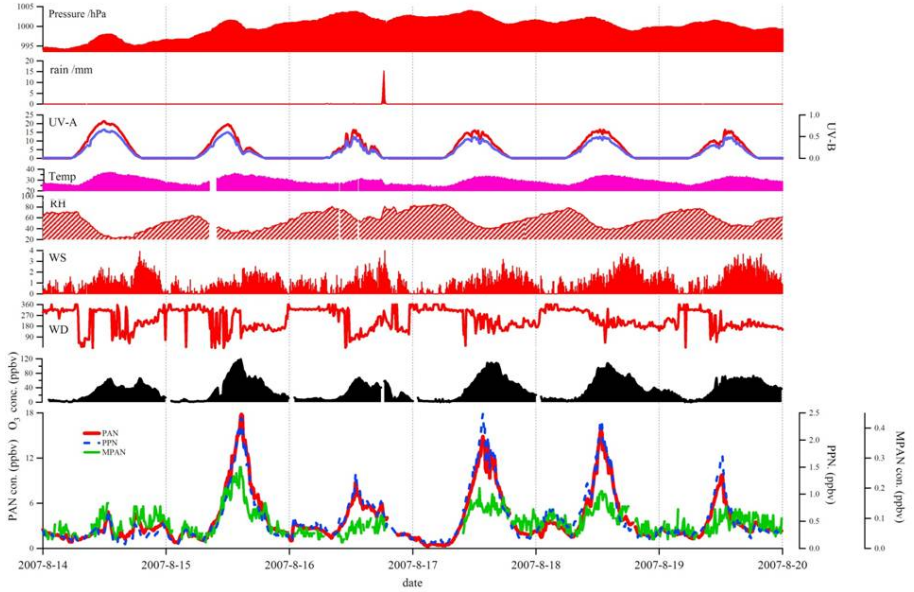

Fig. 2. Meteorological conditions and PAN concentrations from 14 to 19 August 2007 at PKU. WD denotes wind direction, and WS denotes wind speed. The red curve indicates UV-A and its values depend on the left coordinate. The blue curve indicates UV-B, with its value depending on the right coordinate. Intervals indicate either missing data (e.g. power off, in calibration) or low reliability.

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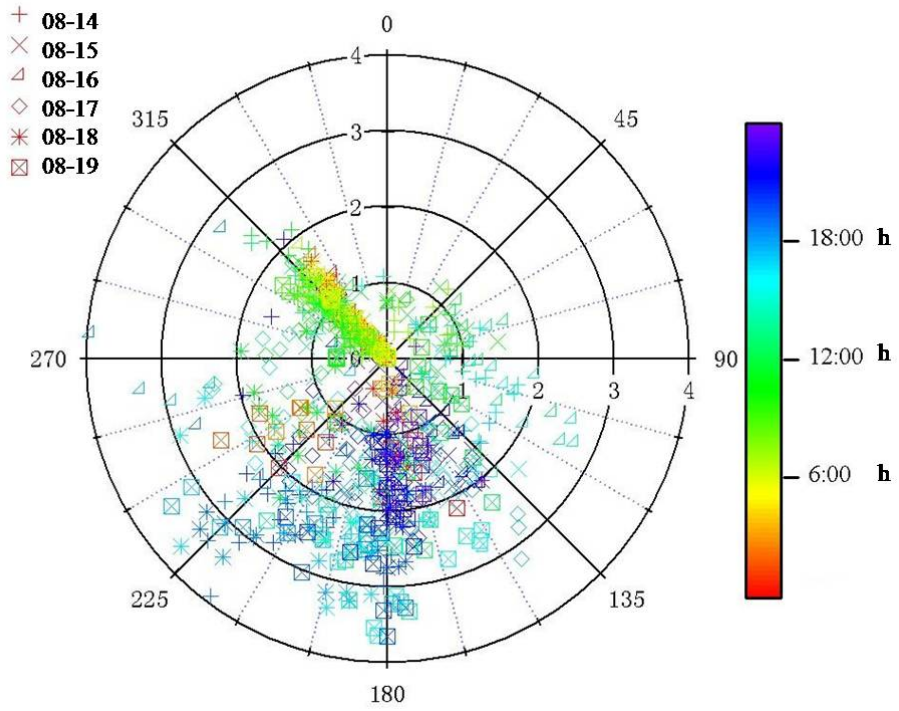

Fig. 3. Relationship between the concentrations of PANs and wind vectors. PAN concentrations vary in color from red to blue with time of day, from 00:00 to 24:00 h. Different symbols represent different sampling days.

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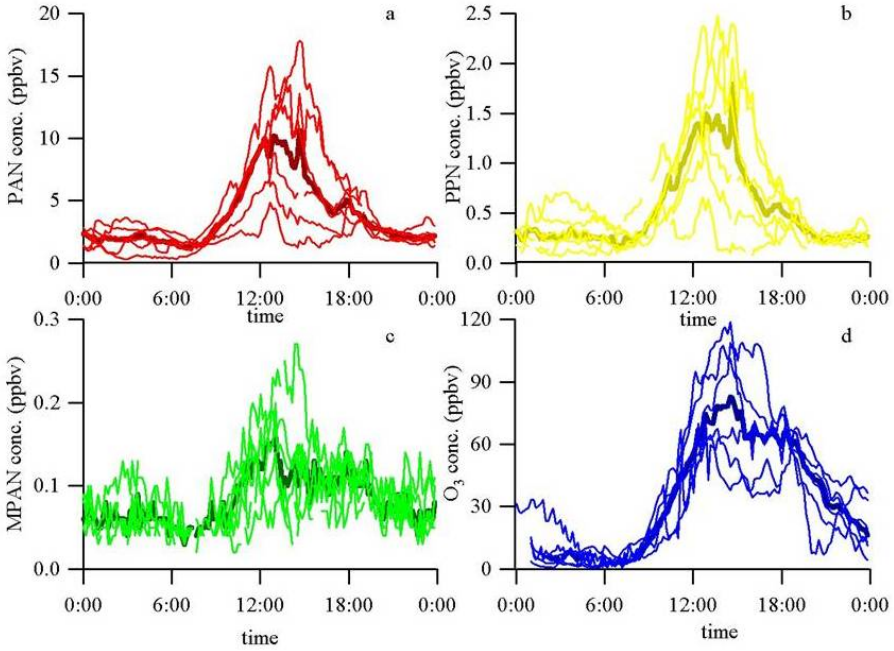

Fig. 4. Diurnal variations in the concentrations of PANs and O_3. The bold curves are plotted based on median values, and single curves represent individual days.

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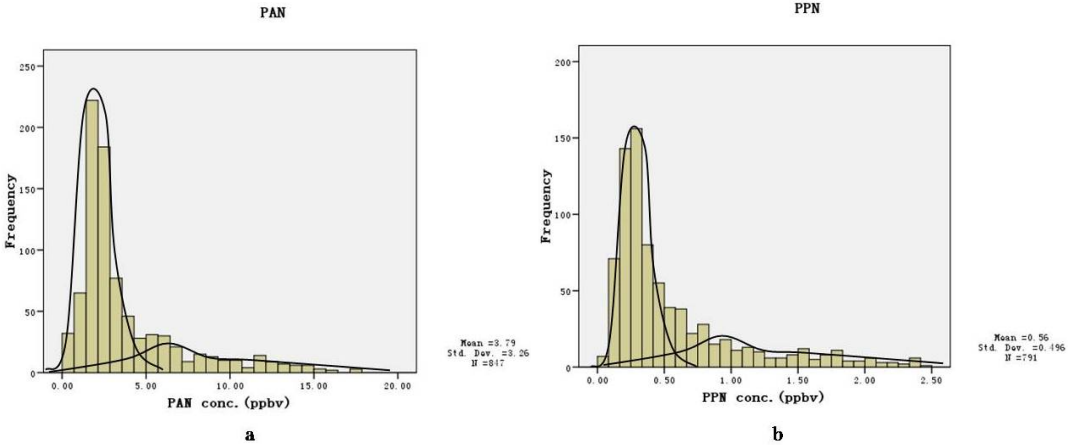

Fig. 5. Frequencies of **(a)** PAN, **(b)** PPN, and **(c)** MPAN concentrations. The black curves indicate potential distribution types.

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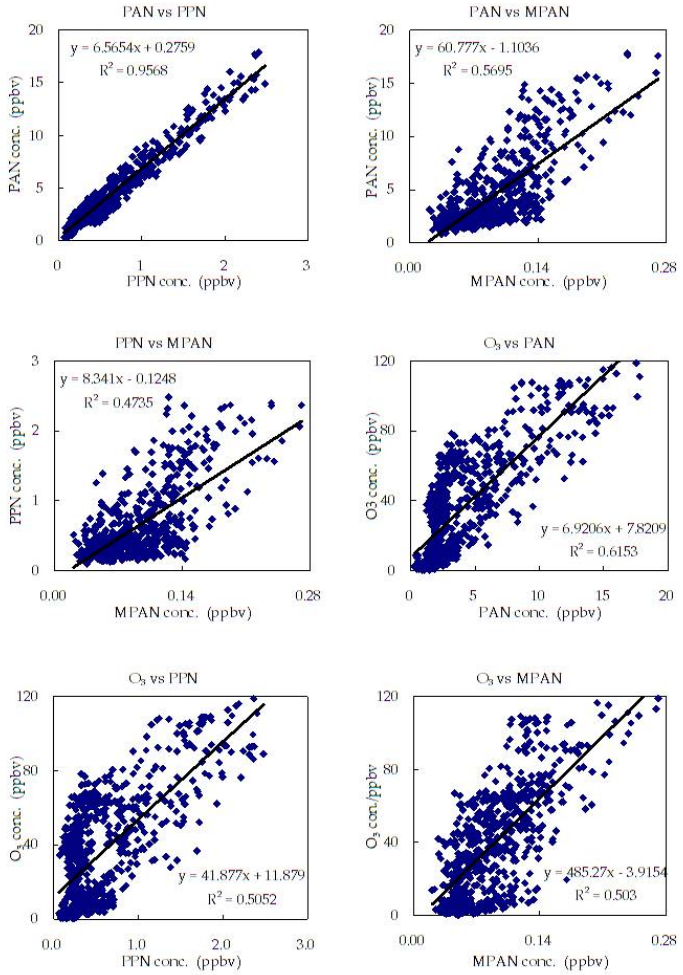

Fig. 6. Correlations among PANs and O_3 during the campaign.

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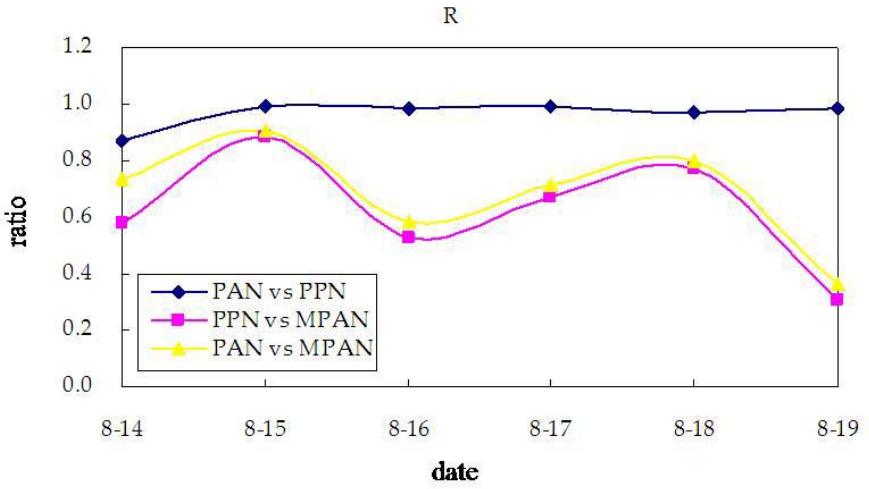

Fig. 7. Correlations among PANs during the campaign.

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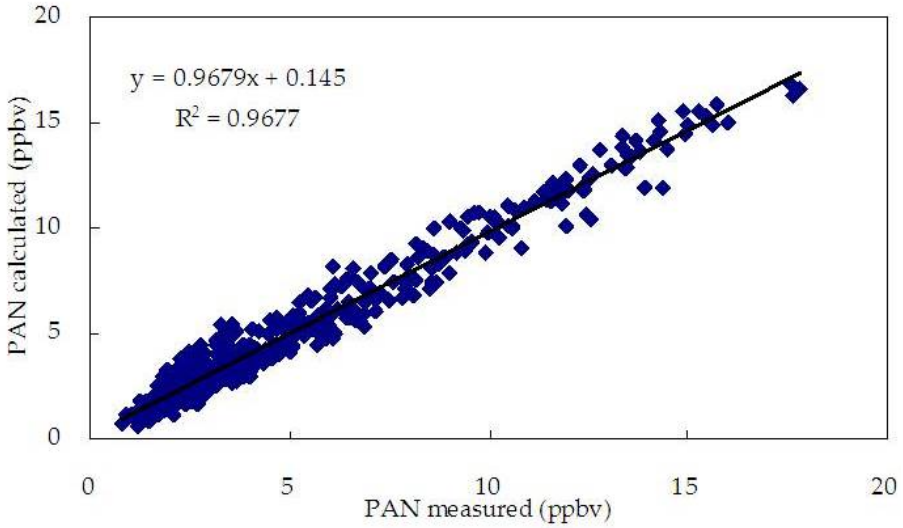

Fig. 8. Correlation between calculated and measured PAN values.

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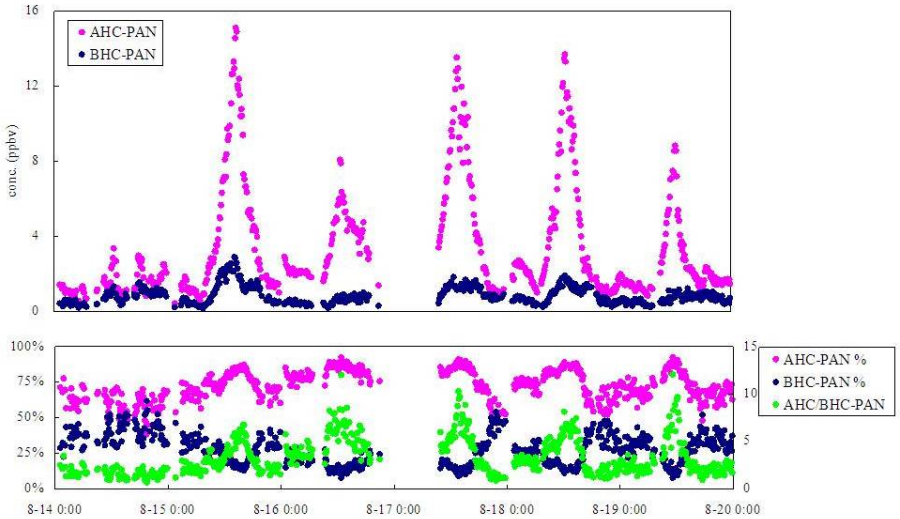

Fig. 9. AHCs, BHCs, and regional mixing background of PAN, estimated from PPN and MPAN levels. Note: The missing data for 17 August at 00:00 h is due to the lack of MPAN data, since PAN data estimates require MPAN data, as shown in Eqs. (1)–(4).

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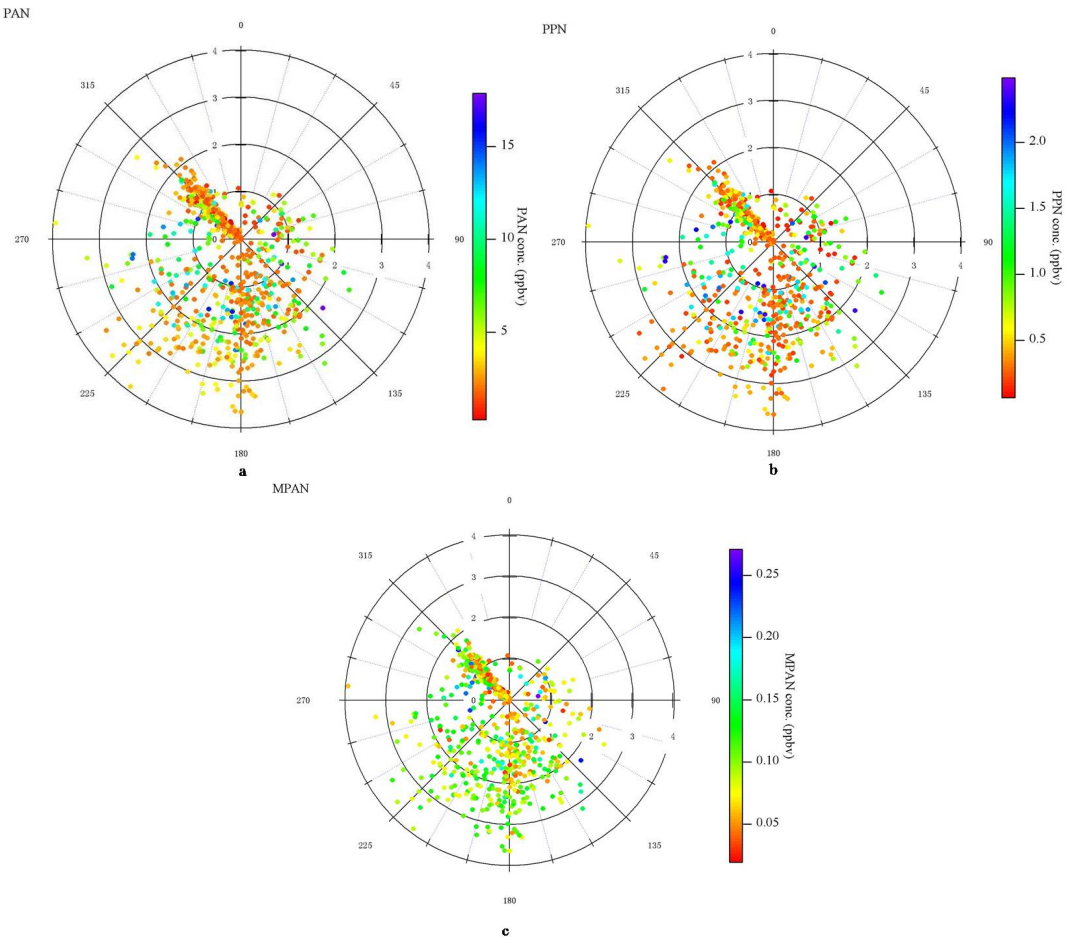

Fig. 10. Relationships between wind direction and PAN concentrations.

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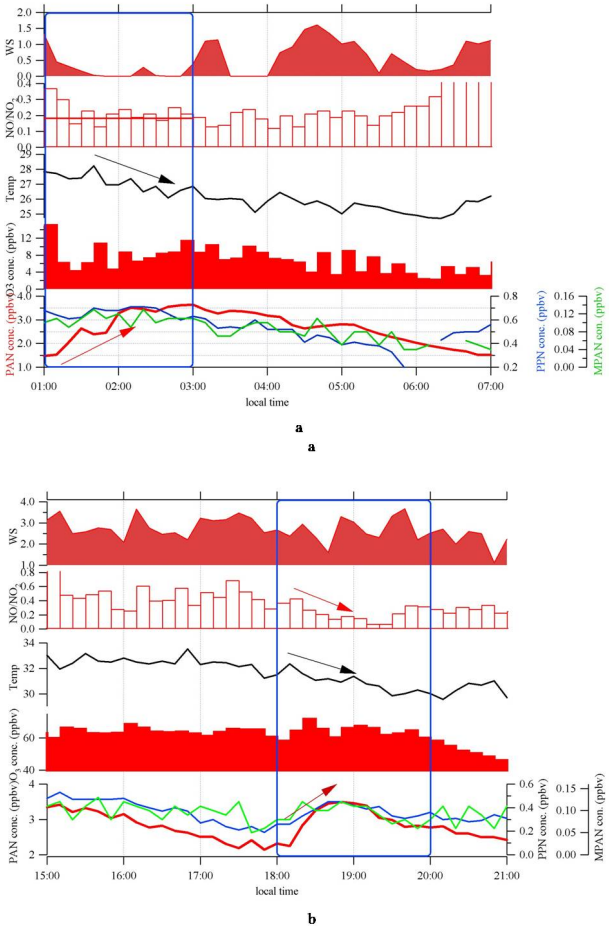

Fig. 11. Case studies of morning and evening peaks of PANs.

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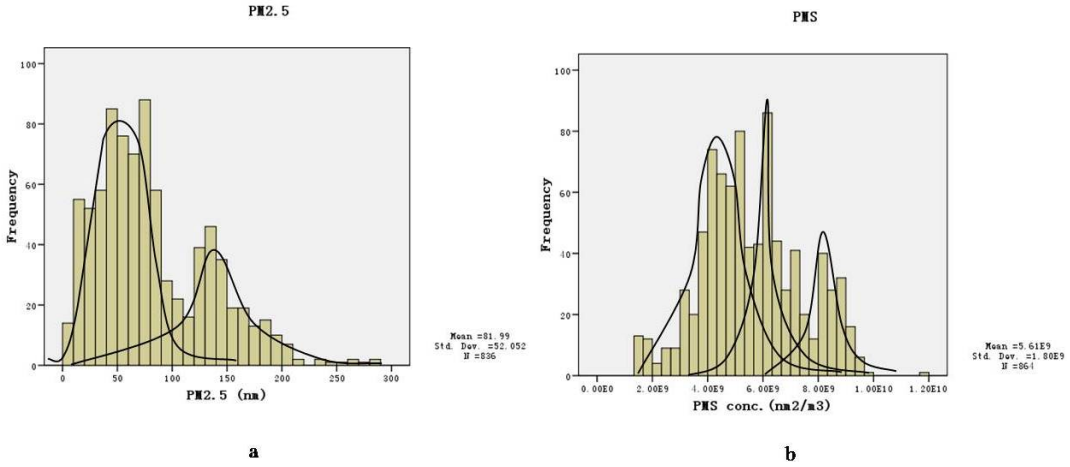

Fig. 12. Frequencies of $PM_{2.5}$ levels and surface concentrations PM_{10} (PMS).

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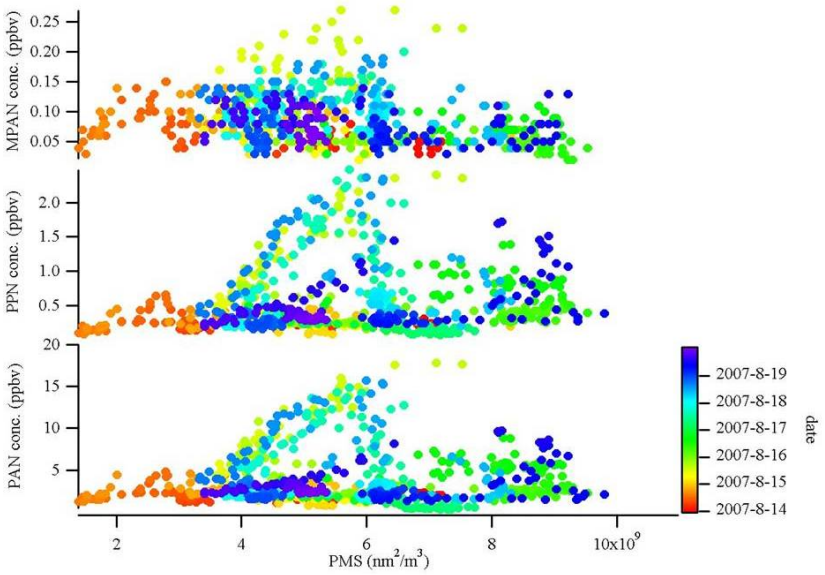

Fig. 13. Correlations between PANs and PMS, classified by day.

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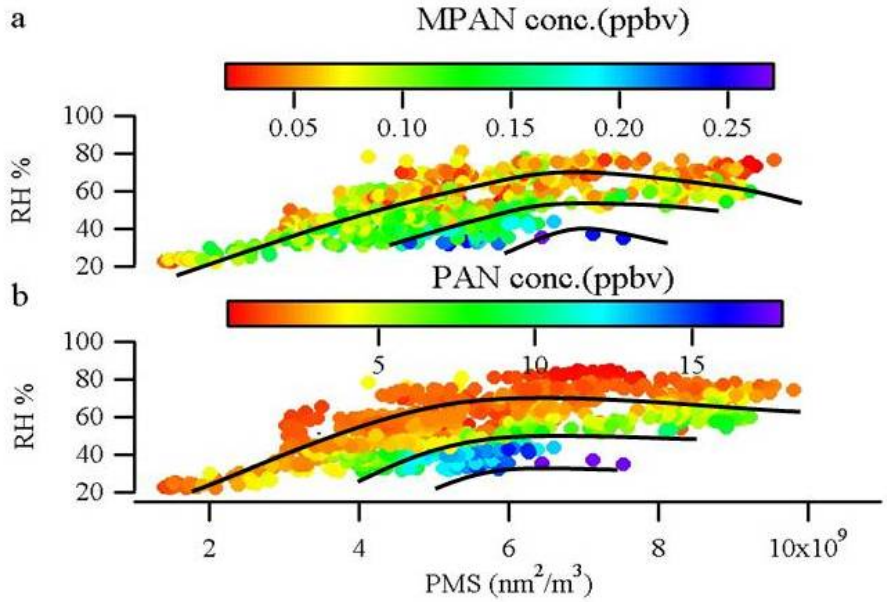

Fig. 14. Relationships of PAN (MPAN) with RH and PMS.

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