**Atmospheric
Chemistry
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Discussions**

Peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN) in urban and suburban atmospheres of Beijing, China

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Abstract

Peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN) were measured sequentially in situ by an online gas-phase chromatograph with electron capture detector at urban (Peking University, PKU) and suburban (Yufa, A town in the south of Beijing) sites in Beijing during the photochemical season in 2006. Maximum and average values of PAN were 11.22 ppbv and 1.95 ppbv at PKU during 15 to 27 August, and maximum and average values of PPN were 2.51 ppbv and 0.41 ppbv at Yufa during 2 to 12 September. Average mixing ratios (PAN/PPN) were 5.60 (at PKU) and 5.83 (at Yufa), which is much lower than those in other metropolitan areas. High correlation between PAN and PPN reflects similar volatile organic compound origins. Thermal loss of PAN and PPN was remarkable when compared with their ambient concentrations. PAN and PPN with ozone have similar trend by day. Thermal decompositions of PAN and PPN were calculated, and results indicated that thermal losses influence their atmospheric lifetime significantly. The percentages of PAN loss at the two sites were very similar; however, PPN urban loss was higher than that in suburban.

1 Introduction

Peroxyacyl nitrates (PANs, $RC(O)OONO_2$) play an important role in tropospheric chemistry and are better indicators of photochemical smog (Carter et al., 1981; Schrimpf et al., 1995) than ozone (Rappengluck et al., 1993, 2003). They are toxic to the environment and can damage plants (Dugger and Ting, 1968; Teklemariam and Sparks, 2004; Temple and Taylor, 1983), irritate human eyes (Dugger et al., 1963), and lead to genetic mutation (Kleindienst et al., 1990). These compounds, especially PAN, are prominent and ubiquitous in the atmosphere. Temperature affects their lifetimes remarkably. For PAN, at −26 °C (the average temperature at 6 km) and NO to NO_2 ratios of ca. 0.1, the lifetime of PAN is 5.36 yrs (Kleindienst, 1994), and at 25 °C, it depletes exhaustively in only 30 min (Bridier et al., 1991). Their stable properties under low temperatures mean

that PAN and PPN can be transported long distances, acting as reservoirs for odd nitrogen compounds, becoming involved in atmospheric circulation, and influencing air quality (Singh et al., 1992a, b) on local, regional, and global-scales.

Gaffney et al. (1999) indicated that PAN and PPN produced in megacities are likely to contribute strongly to regional scale ozone and aerosol production during long range transport. To date, PPN (Grosjean, 2003) has been reported in fewer studies than that for PAN. Only a few studies have reported PAN and PPN in East Asia concurrently (Lee et al., 2008; Sun and Huang, 1995; Zhang and Tang, 1994; Zhang et al., 2009) and no studies on mainland China except Zhang and Tang (1994) done by more than a decade ago. More comprehensive studies have been carried out in North America (Shepson et al., 1992; Singh and Salas, 1989; Williams and Grosjean, 1991), and ambient PAN and PPN have been studied in southern California since 1960 (Grosjean, 2003). No previous in situ simultaneous study of PAN and PPN in Asia has been reported ever before.

To illustrate the status of PAN and PPN pollution in urban and suburban areas and to make comprehensive comparisons with results from other sites, a global summary is provided in Table 1. Since the occurrence of photochemical smog in Los Angeles, California, during the last century, substantial improvements in air quality have been implemented. PAN and PPN pollution have declined significantly in the United States. From its highest level of 58 ppbv, PAN levels have generally dropped to below 10 ppbv, and the average concentration is much lower. Beijing and its surroundings suffer air pollution severely due to photochemical smog (reported high ozone) and aerosol (Ding et al., 2008; Guttikunda et al., 2005) and O_3 episodes have been studied comprehensively there (An et al., 2007; Duan et al., 2008; Xu et al., 2008). However, few studies have been done apart from those on ozone. Therefore, PAN and PPN measurements were conducted both in urban and suburban sites of Beijing during the summer of 2006. The results were provided in the following sections.

2 Methods

2.1 Sampling

Beijing locates in the northwest of the North China Plain and is high in the northwest and low in the southeast. Its west, north, and northeast are surrounded by mountains; its southeast is a gently sloping plain to the Bohai Sea. At the end of 2008, the resident population in Beijing was 16.95 million, which represented a 0.62 million increase over the end of 2007. Beijing had only 2300 motor vehicles in 1949; by 1966, this number had increased to 26 000 and by 1978, it was 77 000. With 10 years of development under policies of reform and outreach, the number of motor vehicles approached 1 million in February 1997, and Beijing has entered a period of rapid development since then. Vehicle exhaust pollution plays pretty important role in Beijing's air quality. In 2006, the total number of motor vehicles was 2.45 million. On 26 May 2007, the number of motor vehicles exceeded 3 million. In recent years, the average annual rates of increase in motorized transport have been generally higher than 10%.

Measurements of PAN and PPN were taken sequentially from the campus of Peking University (PKU; urban) and Yufa (suburban). Sampling sites are shown in Fig. 1. At PKU, the sampling location was on the roof of the Science Building (25 m high, 39°59′20.92″ N, 116°18′25.91″ E). Zhongguancun Street is on the east side of the building. To the north and west of the building are some relatively low-floor teaching buildings, and to the south is Fourth Ring Road. PKU is located in the Zhongguancun area, which is densely populated, with high levels of human activity and heavy traffic. This sampling site should reflect the air pollution in a typical urban area. At Yufa, the sampling location was on the roof of the Main Teaching Building of Huangpu University (15 m high, 39°30′52.63″ N, 116°18′30.49″ E). This is the higher than the surrounding buildings and is ca. 60 km south of PKU. Yufa is in the southern suburbs of the Daxing district, neighboring the Yongding River and on the border of Hebei Province. The site was characterized by high levels of natural vegetation and low local anthropogenic pollutant emissions compared to PKU.

2.2 Equipment

Ambient PAN and PPN were measured using a gas column-electron capture detector (GC-ECD). Detailed information about this instrument can be found in Williams et al. (2000). Briefly, the detector was manufactured by the United States National Oceanic and Atmospheric Administration (NOAA). The column (model DB-210, internal diameter (ID) 0.53 mm, 2 m; J&W Scientific, Folsom, CA) was wrapped around an aluminum block, which was thermoelectrically cooled to 15 °C to minimize the thermal decomposition of PAN and PPN. During sample loading, the oven was also cooled to 15 °C. The volumes of helium (carrier gas) and nitrogen (make-up gas) were at 15 standard cubic centimeters per minute (sccm) and 30 sccm, respectively. Whole-air injections were made from a 2-mL sample loop composed of a PFA (Polytetrafluoro ethylene, commercially named NEOFLON PFA) with an outside diameter (OD) of 1/8 inch. Ambient air at 1 standard liter per minute (slpm) was drawn continuously by a diaphragm pump and sampled by a Teflon sampler at 5-min intervals using a Teflon six-port rotary valve (VICI Valco Instruments Co. Inc., Houston, TX) automatically. The ECD used was a ^{63}Ni model maintained at 40 °C. The detection limits for PAN and PPN were 5 and 10 parts per trillion by volume (pptv), respectively, with uncertainties (2σ).

All inlets (less than half a meter long with the diameter of 6 mm) were made of Teflon to minimize the loss of PAN and PPN and to prevent heterogeneous formation. Gaseous PAN was prepared directly through the reaction of CH_3COCH_3 with NO under ultraviolet (UV) light (wavelength, 285 nm). It is diluted for calibration. The diluted concentration of PAN ranges from couple of pptv to ca. 15 ppbv to cover the range of ambient PAN concentration. PPN was synthesized in liquid phase in laboratory and then volatilized. These preparations were used for instrument calibration. The ECD's response to PPN was 0.83 when compared to the PAN response, which was set equal to 1.0. The value of 0.83 is from Roberts' studies (1998, 2003a, b, 2007). Calibration was performed before and after the measurement period, and no significant changes were observed. The system was also calibrated before and after the in situ sampling.

Overall uncertainty was 15% for PAN and 20% for PPN. The in situ sampling at PKU and Yufa took place from 15 to 27 August and 3 to 12 September, respectively.

While PAN and PPN measurements were being taken, ozone (It was calibrated by situ standard ozone) was also measured (this stopped on 11 September 2006 at Yufa) using an analyzer (EC9810 Ozone analyzer, ECOTECH) with a detection limit of 1 part per billion by volume (ppbv). NO_x were measured using a high-sensitivity NO_x analyzer (EC9841 $NO/NO_2/NO_x$ analyzer, ECOTECH) with a detection limit of 0.4 ppbv. Both instruments were dynamically calibrated using a dynamic calibrator. Since the chemiluminescent NO_x analyzer measures the sum of NO_2, NO, PAN, PPN, etc. (Steinbacher et al., 2007; Winer et al., 1974), the NO_2 mixing ratio was estimated by subtracting the mixing ratios of NO, PAN, and PPN from the total NO_x level (Carter et al., 1981). As a preliminary study into the relationships between PAN and PPN and their primary volatile organic compounds (VOCs), some species (n-butane, trans-2-butene, 1-butene, cis-2-butene, and propylene) were measured with a time resolution of 1 h. The method (EPA's Method TO-15) specifies steps for collecting samples of ambient air in passivated stainless steel canisters and analyzing them using a gas chromatograph (Shimadzu Mini-2) with flame ionization detection. The canisters were cleaned and evacuated before being placed at the sampling sites.

After cleaning, the canisters were analyzed for the presence of VOCs to verify that they were clean before final evacuation and the initiation of the next sampling event. Ambient air samples were pre-concentrated by a multiadsorbent technique and then analyzed using a gas chromatograph with a flame ionization detector. The detection limits were about 0.1 ppbv.

All examined pollutants and corresponding meteorological parameters (including temperature, RH, pressure, wind speed, wind direction, levels of UV-A and UV-B light, and precipitation) were measured continuously from the same height as were PAN and PPN (at Yufa, meteorological observation stopped on 13 September). Any breakpoints in the following time series were due to power outages or calibration.

3 Results and discussion

3.1 Time series of PAN and PPN

PAN and PPN were measured at PKU from 15 August to 27 August 2006 and at Yufa from 3 to 12 September 2006, and the results are shown in Fig. 2. The variations in PAN, PPN, and ozone (in Fig. 2a and b) basically follow the same trends (Stephens 1973, Taylor 1969). PAN and O3 are highly correlated in aged air masses as both are secondary pollutants. Major statistical data are shown in Table 2.

At PKU, the maximum concentration ratio of PAN to PPN and PAN to $O_3 (\times 10^2)$ for each day during this short campaign ranged from 4.70–7.52 (average 5.64 ± 0.62) and 0.25–0.81 (average 0.51 ± 0.14). At Yufa, the maximum ratio of PAN to PPN and PAN to O_3 ($\times 10^2$) ranged from 4.99–7.25 (average 6.04 ± 0.73) and 0.13–0.26 (average 0.20 ± 0.04). PAN and PPN were lower than O_3; the PAN concentration was consistently higher than that of PPN. These findings are in accord with PAN and PPN measurements taken from other places (Grosjean, 2003; Lee et al., 2008; McFadyen and Cape, 2005; Roberts et al., 2007; Zhang et al., 2009).

During the sampling period, the maximum concentrations of PAN and PPN at PKU both occurred on 24 August (see Fig. 2). At Yufa, the maximum concentrations of PAN and PPN were on 6 September, and the peak level of O_3 on that day was much higher than the levels regularly observed, up to 114 ppbv (see Fig. 2). However, occasional discrepancies did occur on some days, such as at PKU on 20 August, when PAN and PPN showed no diurnal variation, while O_3 fluctuations followed their usual pattern. This is discussed in Sect. 3.2. Tiny peaks for PAN, PPN, and O_3 were observed at midnight on 19, 22, 24 and 25 August at PKU and 7 and 12 September at Yufa.

As shown in Fig. 2c, when comparing the statistical parameters of PAN, PPN and ozone, we found that levels of PAN and PPN were higher in 2006 than those in 2005 (Wang and Zhang, 2007). Ozone levels were lower in the first quartile of 2006 than they were in 2005, but were otherwise higher in 2006. PAN showed the greatest increase (158 %), followed by PPN (118 %) and O_3 (15 %). PAN concentrations over 10 ppbv

were observed for the first time in Beijing. The maximum concentrations of PAN and PPN measured in the summer of 2006 were about 3 times higher than those measured at PKU in the summer of 2005, when the maximum concentration of PAN was 2.49 ppbv and that of PPN was 0.51 ppbv. In urban Beijing, PAN and PPN pollution had increased in 2006 compared with 2005. Levels of PANs pollution in Beijing are still much lower than those recorded from Los Angeles, California, during the 1960s and 1970s (70 ppbv) (Grosjean et al., 2001) and from Mexico City in 1997 (34 ppbv) (Gaffney et al., 1999). As shown in Fig. 3, higher concentrations of PAN and PPN were generally associated with southerly winds, which are conducive to pollutant stagnation. The number of vehicles in Beijing continues to increase, so does off-gassing (NO_x + VOCs). According to information from the Traffic Authority of Beijing Municipal Public Security, Beijing is experiencing a rapid increase in vehicle numbers. In 2006, 370 000 motor vehicles were put into use, causing a net increase of 287 000, and by the end of 2006, the total number of motor vehicles in Beijing had reached 2.45 million. Concern about the health effects of PANs and their potential damaging effects on vegetation prompted the World Health Organization (WHO) to set an air quality guideline of 5 ppbv over 8 h for PANs (WHO, 1987). During our study period, PAN levels did not exceed this guideline; however, extensive attention should be focused on the contribution of traffic to photochemical pollution.

With increasing economic development and urbanization, and given the geographical terrain (the city is surrounded on the west, north, and northeast by mountains that impede the diffusion of pollution), Beijing is at risk for increasing pollution levels. In order to characterize the effects of wind direction and wind speed on pollutants, wind roses were plotted as shown in Fig. 3.

As shown in Fig. 3, the effects of wind on PAN and PPN followed similar patterns at both sites. Higher mixing ratios of PAN and PPN mainly related to south or southwest wind directions. Pollution became serious when the wind speed was less than $4\,\mathrm{m\,s^{-1}}$.

In this study, we analyzed relationships between PAN and PPN with their major VOC precursors. Because propylene (Chang and Tso, 1994; Kleindienst, 1994) and total

butene, including n-butane, trans-2-butene, 1-butene, and cis-2-butene (Gaffney et al., 1999; Kleindienst, 1994), accounted for an important proportion of PAN and PPN formation, a time series of PAN and PPN with propylene and total-butene at PKU Site was plotted in Fig. 4, showing negative correlation.

When compared with other sites, PAN and PPN pollution at PKU is not particularly high, but the overall pollution levels in Asia are high relative to those of other regions worldwide. High mixing ratios mainly occur in Mexico City, Santiago de Chile, Sao Paulo, and some Asian cities, which are undergoing rapid urbanization or are being influenced by surrounding areas. Current levels of PAN pollution are a little higher than the maxima of 6.8 ppbv when comapred to that in 1990s. The suburban Yufa site was lightly polluted. PAN pollution at the Yufa site was not much higher than background levels of PAN recorded from Mt. Waliguan in China, and it was even lower than levels recorded from Lanzhou. PAN concentrations at this background site were an order of magnitude higher than those recorded from a background site at Chebogue Point, Nova Scotia, North Atlantic. Zhang et al. (2009) demonstrated that PAN mixing ratios at Mt. Waliguan may be influenced by Lanzhou and other surrounding areas. A cruise around Charleston, South Carolina, also measured relatively high levels of PAN pollution. With back trajectory, it was demonstrated that mainland transportation resulted high levels of PAN pollution at sea (Rappengluck et al., 2003, 2004; Roberts et al., 2007).

3.2 Diurnal variations in PAN and PPN

Diurnal variations in PAN and PPN levels (as shown in Fig. 5) were similar to those reported from other sites worldwide (Corkum et al., 1986; Evmorfopoulou and Glavas, 1998; Lee et al., 2008; McFadyen and Cape, 2005; Penkett et al., 1975; Rappengluck et al., 1993; Roberts et al., 1998b, 2007; Schrimpf et al., 1998; Shepson et al., 1992; Stephens, 1973; Tsanibazaca et al., 1988; Williams and Grosjean, 1990). After sunrise and the morning rush hour, precursors for PAN and PPN formation (such as VOCs and NO_x) increased, leading to gradual increases in PAN and PPN concentrations, which

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reached their maximum levels during the afternoon, thereafter slowly decreasing to their minima at about midnight (see Fig. 5).

The daytime peak at PKU was similar to that measured at Yufa. Strictly, there were two peaks during the day, but the second peak was not clear. The peak always occurred after 15:00, as shown in Fig. 5a and b. During the night, two peaks were observed for PAN and PPN, before and after 00:00, which were different from those measured at Yufa. The afternoon peaks for PAN and PPN were probably due to the heavy work-related traffic. Although sunlight is not particularly strong by the mid-afternoon, emission of pollutants (such as NO_x) was heavy, resulting in the afternoon peak. At Yufa, which is suburban, vehicle contributions to pollution were less important than they were at the urban site of PKU.

At Yufa, PAN and PPN concentrations increased rapidly from 08:30 through photochemical reaction, and they reached their daytime maxima between 12:00 and 15:00. After this first peak, PAN and PPN concentrations initially fell until the downward trend reversed to approach a second peak between 18:00 and 21:00. After 20:30 when the sun had set, PAN and PPN concentrations gradually declined. At about 00:00, there was a slight increase to a short peak, before a gradual drop to early morning.

3.3 Correlations between PAN, PPN and O_3

The VOC precursors of PAN were unlike those of PPN. PAN precursors are generators of $CH_3CO_3\cdot$, which originates from both biological and anthropogenic sources, whereas PPN precursors are those that generate $CH_3CH_2CO_3\cdot$, which originates almost exclusively from anthropogenic sources (Grosjean et al., 1993, 2001; Grosjean, 2001; Roberts et al., 2004). The main VOC sources can be inferred based on the concentration ratios of PPN to PAN (Roberts et al., 2004).

PAN and its analogues have relatively similar chemical properties. Their thermal stabilities are also basically the same. Linear regression between PAN and PPN at PKU is shown in Fig. 6a [PAN] = 5.60[PPN] + 135 pptv, ($R^2 = 0.98$, $n = 3678$). Williams et al. (1998) and Roberts et al. (1998b, 2001) demonstrated that when the regression

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slope was less than 7.4, photochemical processes in the area were primarily influenced by anthropogenic hydrocarbons (AHCs). A steeper slope indicated that the percentage of AHCs participating in photochemical reactions was much higher. Roberts et al. (1998a, 2001) and Williams et al. (1998) indicated that ratios of PAN to PPN ranging from 5.8 to 7.4 reflected AHC-dominated photochemical reactions. At PKU, the ratios of PAN to PPN ranged from 4.70 to 7.52, suggesting that AHCs dominated local photochemical processes. PAN and PPN measurements were also taken during 13–28 August 2005, and the correlation between PAN and PPN was found to be [PAN] = 4.98[PPN] − 19 pptv, ($R^2 = 0.95$, $n = 3459$).

The linear regression between PAN and PPN at Yufa is shown in Fig. 6b: [PAN] = 5.83[PPN] + 77 pptv, ($R^2 = 0.93$, $n = 2841$). Ratios of PAN to PPN ranged from 4.99 to 7.25 and were considerably lower than 7.4, indicating that photochemical processes at Yufa were also mainly controlled by AHCs. However, the effect of AHCs at Yufa was weaker than it was at PKU, and biological hydrocarbons (BHCs) also contributed partly. Yufa is located in the suburbs of Beijing, and although there were not many vehicles in the area, it neighbors the Jingkai Highway Express. Vehicles had a great impact on pollution at the site, and AHCs still dominated local photochemical processes.

PAN is a product of photochemical smog, and tropospheric O_3 also comes primarily from photochemical reactions of NO_x (NO and NO_2) generated by vehicle and industrial emissions. Therefore, variations in PAN and ozone tend to be closely correlated (Schrimpf et al., 1998). The linear regression for O_3, PAN, and PPN at PKU was described as [O_3 (ppbv)] = 18.87[PAN (ppbv)] + 6.88, ($R^2 = 0.65$, $n = 3400$); [O_3 (ppbv)] = 9 9.00[PPN (ppbv)] + 11.64, ($R^2 = 0.56$, $n = 3306$). At Yufa, the correlation for O_3, PAN, and PPN was [O_3 (ppbv)] = 42.94[PAN (ppbv)] + 4.92, ($R^2 = 0.59$, $n = 2205$); [O_3 (ppbv)] = 234.09[PPN (ppbv)] + 8.95, ($R^2 = 0.51$, $n = 1994$).

Based on our measurements, the correlation between PAN and O_3 was not significant (see Fig. 7). The correlation coefficients were 0.65 and 0.59 at PKU and Yufa, respectively. The main reasons for this finding can be summarized as follows:

Different chemical formation and removal processes. During the day, net O_3 production occurs through the following reactions (Roberts et al., 1995):

$$HO_2 + NO \rightarrow OH + NO_2$$

$$RO_2 + NO \rightarrow RO + NO_2$$

$$NO_2 + hv \rightarrow NO + O$$

$$O + O_2 \rightarrow O_3$$
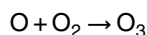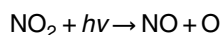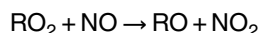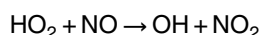
VOC precursors for PAN can transfer to aldehyde vinyl substances with CH_3CO, such as acetaldehyde and acrylamide. The subsequent reaction is $CH3O \cdot + O_2 \rightarrow CH_3C(O)OO \cdot$,

$CH_3C(O)OO \cdot + NO_2 \rightarrow CH_3C(O)OONO_2$(PAN). In the removal process, O_3 mainly reacts with NO, whereas PAN is mainly removed by thermal decomposition, the rate of which is determined by temperature and NO/NO_2 ratios (Tuazon et al., 1991).

Heterogeneous reactions take place on aerosol surfaces, which can reduce tropospheric O_3 concentration by directly or indirectly adsorbing O_3 precursors (NO_x and VOCs) (Jia et al., 2006). In addition, the stability of PAN and PPN is weaker than that of O_3, which also has external input from the atmospheric boundary layer exchange. PAN and PPN have no natural emission sources and are only generated by human activities.

The relationship between ozone and PAN is discussed separately by daytime (08:00–20:00) and nighttime (20:00–08:00). The relationship of PPN with ozone was similar to that of PAN with ozone, except for magnitude differences, and has therefore been omitted from this discussion. PAN and O_3 were well correlated during the day, but the correlation was much weaker at night. This is mainly because PAN (PPN) and O_3 are

primary integral parts of photochemical smog, which is generated to a large extent by photochemical reaction effected by light, especially by the short-wave bands found during the day. At night, light is insufficient for photochemical reactions such as PAN and ozone formation. During nighttime, decomposition (sink) becomes very important, and PAN (PPN) and O_3 vary from each other in their decomposition mechanisms (Roberts et al., 1995).

PAN and PPN were strongly correlated both during the day and at night (see Fig. 8), with only slightly different slopes. Since PAN and PPN are very similar at the structural level, both their reaction and decomposition mechanisms are alike, with only a minor difference in rate constants.

3.4 Thermal decomposition of PAN and PPN

PAN and PPN have three main sink pathways: dry deposition, surface reaction, and thermal decomposition. Thermal decomposition is the main pathway by which PAN and PPN are removed from the atmosphere.

PAN was generated by acetyl-peroxynitrite ($CH_3C(O)OO\cdot$) and NO_2:

$$CH_3C(O)OO\cdot + NO_2 \rightarrow CH_3C(O)OONO_2 \tag{1}$$

Acetyl-peroxynitrite can be generated by a broad species of organic compounds. Reaction (R1), leading to PAN formation, was competitive with Reaction (R2), showing the reaction of acetyl-peroxynitrite with NO:

$$CH_3C(O)OO\cdot + NO \rightarrow CH_3C(O)O\cdot + NO_2 \tag{2}$$

$$CH_3C(O)O\cdot \rightarrow CH_3\cdot + CO_2 \tag{3}$$

Thermal decomposition of PAN in the atmosphere was also important:

$$CH_3C(O)OONO_2 \rightarrow CH_3C(O)OO\cdot + NO_2 \tag{4}$$

Reaction (R4) was considerably active at room temperature, and the reaction rate increased rapidly when the temperature increased. This was the most important of the PAN sink pathways (Talukdar et al., 1995).

Based on Reactions (R2–R4), the thermal decomposition rate of PAN mainly depended on temperature and on the concentration ratio of NO to NO_2. The rate of thermal decomposition can be calculated as follows:

$$-\frac{d\ln[PAN]}{dt} = \frac{k_2 k_4[NO]}{k_2[NO] + k_1[NO_2]} \tag{5}$$

In which, k_1, k_2, and k_4 are the reaction constants for [PAN], [NO], and [NO_2], respectively. When temperature ranged from 10–40 °C, at standard atmospheric pressure, $k_{4-PAN} = 2.52 \times 10^{16} e^{-13573/T}$ s^{-1}, $k_{2-PAN}/k_{1-PAN} = 1.95 \pm 0.28$ (Tuazon et al., 1991) and $k_{6-PPN} = 7.94 \times 10^{16} e^{-13940/T}$ s^{-1} (Kirchner et al., 1999). Equation (5) can be simplified as

$$-\frac{d\ln[PAN]}{dt} = \frac{k_{4-PAN}}{1 + \frac{[NO_2]}{1.95[NO]}} \tag{6}$$

$$-\frac{d\ln[PPN]}{dt} = \frac{k_{4-PPN}}{1 + \frac{k_{1-PPN}[NO_2]}{k_{2-PPN}[NO]}} \tag{7}$$

For $C_2H_5C(O)OO$:

$$C_2H_5C(O)OO + NO_2 + M = PPN + M \tag{8}$$

Low pressure limit: $9.00^E - 28(300/T)^{8.9}$
Hgh pressure limit: $7.70^E - 12(300/T)^{0.2}$

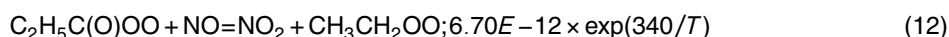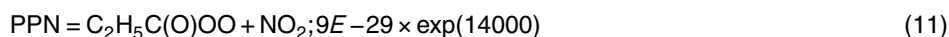F_c: 0.6, see JPL06 http://jpldataeval.jpl.nasa.gov/download.html and IUPAC, http://www.iupac-kinetic.ch.cam.ac.uk/

The equations for the rate constant of Reaction (R8) are shown as follows:

$$k_r = \frac{k_{\infty,T}k_{0,T}[M]}{k_{\infty,T}+k_{0,T}[M]}F_c^{\left[1+\left(\lg\frac{k_{0,T}[M]}{k_{\infty,T}}\right)^2\right]^{-1}} \tag{9}$$

$$[M] = N_d = 6.02E+23\left(\frac{PV}{RT}\right), \text{molec cm}^{-3} \tag{10}$$

PPN thermal decomposition and the reaction between $C_2H_5C(O)OO$ and NO are shown in Eqs. (11) and (12)

$$PPN = C_2H_5C(O)OO+NO_2; 9E-29 \times \exp(14000) \tag{11}$$

$$C_2H_5C(O)OO+NO = NO_2+CH_3CH_2OO; 6.70E-12 \times \exp(340/T) \tag{12}$$

Therefore, $k_{\text{C2H5C(O)OO-NO}} = 6.70 \times 10^{-12} \times e^{\frac{340}{T}}$ \tag{13}

Namely,

$$\frac{k_{\text{C2H5C(O)OO-NO}}}{k_{\text{C2H5C(O)OO-NO}_2}} = \frac{6.70\times10^{-12}\times e^{\frac{340}{T}}}{\frac{7.70\times10^{-12}(\frac{300}{T})^{0.2}\times9.00\times10^{-28}(\frac{300}{T})^{8.9}\times6.02\times10^{23}\times(\frac{PV}{RT})}{7.70\times10^{-12}(\frac{300}{T})^{0.2}+9.00\times10^{-28}(\frac{300}{T})^{8.9}\times6.02\times10^{23}\times(\frac{PV}{RT})}\times0.6^{\left[1+\left(\lg\frac{9.00\times10^{-28}(\frac{300}{T})^{8.9}\times6.02\times10^{23}\times(\frac{PV}{RT})}{7.70\times10^{-12}(\frac{300}{T})^{0.2}}\right)^2\right]^{-1}}}$$

Unlike levels of PAN at the two sites, the ratios of $k_{2-\text{PPN}}/k_{1-\text{PPN}}$ were very different at two sites, namely 2.80 ± 0.03 at PKU site and 3.22 ± 0.096 at Yufa site.

During the measurement period, the temperature ranged from $18.7\,°C$ $-37.1\,°C$ at PKU and from $10.1\,°C–29.8\,°C$ at Yufa, which was within the reference referred range of $10\,°C–40\,°C$. Thermal decomposition of PAN and PPN can therefore be calculated according to the relevant equations.

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High correlations in the percentages of thermal decomposition of PAN and PPN are shown in Fig. 9a and b. The slope was less than 1, indicating that the relative thermal loss of PPN was more than that of PAN. The ratio of k_1/k_2 was smaller for PAN than for PPN; thus, NO was more important in the thermal loss of PPN than in that of PAN. The absolute values of PAN and PPN thermal loss were also correlated (see Fig. 9c and d), although the coefficient at Yufa was lower than that at PKU. For PPN, the slope at Yufa was larger than that at PKU and showed poor correlation. For PAN, there was little difference between the two sites. When comparing PAN thermal loss versus PPN thermal loss, it was found that the coefficient at PKU was higher than that at Yufa, indicating that plots at Yufa were more disturbed.

PAN and PPN thermal decomposition was calculated (see Table 3), and the results indicate that thermal loss has an important impact on their atmospheric lifetime. The percentages of PAN loss at the two sites are roughly the same; however, for PPN, urban loss was higher than suburban. TDPAN and SUM represent the thermal decomposition of PAN and the adding of it with correspding ambient concentration.

4 Conclusions

When compared with data gathered from PKU in 2005, it was found that both PAN and PPN levels had increased in 2006. Inverse correlations between PAN, PPN, and their major VOCs were found. Diurnal variations in the levels of PAN and PPN accorded with the characteristics of photochemical reactions. Correlation showed that PAN and PPN levels appeared to follow generally similar trends, with a strong correlation coefficient ($R^2 = 0.93 - 0.98$). The ratio between PAN and PPN ranged from 4.6 to 7.4, indicating that the main contributors to VOCs at both sites were AHCs. PAN and PPN thermal decomposition was calculated, and the results confirmed that thermal loss has an important impact on their atmospheric lifetimes. The percentages of PAN loss at the two sites were broadly the same; however, for PPN, the urban site showed higher percentage losses than did the suburban site.

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Long-term measurement of PAN, PPN, NO, NO$_2$, O$_3$, and other pollutants is recommended to further increase understanding of the photochemical pollution in Beijing and its characteristics. Based on on-line monitoring data, reasonable methods and strategies can be implemented to improve air quality and curb the spread of photochemical pollution.

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Table 1. Comparison of PAN and PPN levels measured in this study with those measured in other regions (ppbv).

Site	Type	Date	PAN ppbv (max/aver.)	PPN ppbv (max/aver.)	Reference
PKU, Beijing, China	urban	15–27 August 2006	11.22/1.41	1.95/0.24	This study
	urban	Several days in May and June 1990	6.8	–	Zhang and Tang (1994)
Seoul Metropolitan area, Korea	urban	May to July, 2004 and 2005	10.4/0.8	–	Lee et al. (2008)
Taipei, China	urban	July 1992–April 1993	27	–	Sun and Huang (1995)
Houston, Texas	urban	2000	14	–	Roberts et al. (2002)
Athens, Greece	urban	2001	6.6	–	Glavas and Moschonas (2001)
Santiago, Chile	urban	September 2002	3.9/2.8	–	Rubio et al. (2005)
		October 2002	3.8/1.8	–	
		December 2002	9.8/5.3	–	
		January 2003	22/6.4	–	
Riverside, California	urban	Lack data	50	~6	Darley et al. (1963)
		1 August–31 December 1967	58	–	Taylor (1969)
		August 1968	28/5.9	–	
		August 1976	20/3.0	–	
		August 1980	22/5.6	–	Temple and Taylor (1983)
Los Angeles, California	urban	9–21 April 1979	2.7/0.72	–	Singh and Hanst (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, California	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	
Simi Valley, California	urban	July 18–October 16, 1997	3.0/0.608	0.28/0.13	Aneja et al. (1999)
Yufa, Beijing, China	suburban	3–12 September 2006	2.50/0.60	0.41/0.09	This work
Lanzhou, China	suburban	23 June–17 July 2006	9.13/0.76	–	Zhang et al. (2009)
La Vergne Tennessee	suburban	June–July 1995	2.14/0.48	0.32/0.005	Nouaime et al. (1998)
La Porte Airport, Houston, Texas	suburban	August–September 2000	6.5	–	Roberts et al. (2003)
Cornelia Fort Air Park, Tennessee	suburban	14 June–14 July	2.51/0.674	0.43/<0.005	Roberts et al. (2002)
Mt. Waliguan, China	Background	22 July–16 August 2006	1.4/0.44	–	Zhang et al. (2009)
Chebogue Point, Nova Scotia, North Atlantic	Background	August–September 1993	0.325/0.049	0.089/0.009	Roberts et al. (1998b)
Charleston, South Carolina	marine	12 July–10 August 2002	2.79/0.36	0.387/<0.004	Roberts et al. (2007)

Table 2. Statistical data for PAN, PPN, and O_3.

Site	PAN (ppbv)			PPN (ppbv)			Ozone (ppbv)		
	Average	Median	Daily max. range	Average	Median	Daily max. range	Average	Median	Daily max. range
PKU	1.34 ($n=3740$)	0.91	1.21–11.22	0.24 ($n=3239$)	0.15	0.16–1.95	34.59 ($n=3400$)	22.9	39.2–140.4
Yufa	0.60 ($n=2673$)	0.50	0.68–2.51	0.10 ($n=2462$)	0.08	0.13–0.41	31.43 ($n=2234$)	28.6	39.1–114.8

Notes: At PKU, measured PAN was always above the detection limit, but the minimum PPN was sometimes lower than the detection limit (5 pptv). At Yufa, the minimum level of PAN was 0.07 ppbv, and for PPN, the minimum was lower than the detection limit.

Table 3. Summary of data for TDPAN and TDPAN/SUM.

	Site					
	PKU			Yufa		
	PAN: $n = 1575$; PPN: $n = 1476$,			PAN: $n = 2096$; PPN: $n = 1899$,		
	(10 min resolution)			(5 min resolution)		
Thermal decomposition	Max (ppbv)	Min	Average	Max (ppbv)	Min	Average
TDPAN (ppbv)	1.37	<5 pptv	0.13	0.58	1 pptv	0.08
TDPPN (ppbv)	0.31	<5 pptv	0.03	0.04	–	4 pptv
TDPAN/PAN$_{ambient}$	34.1%	–	9.1%	29.2%	0.2%	9.2%
TDPPN/PPN$_{ambient}$	42.2%	0.1%	10.8%	15.24%	–	3.5%

Notes: PAN and PPN data were synchronized with the time resolution of meteorological data and conventional gases at each site (PKU: 10 min; Yufa: 5 min) for thermal loss calculation, resulting in different sampling sizes between the two sites. When calculating thermal loss, 10 min data were used for both sites.
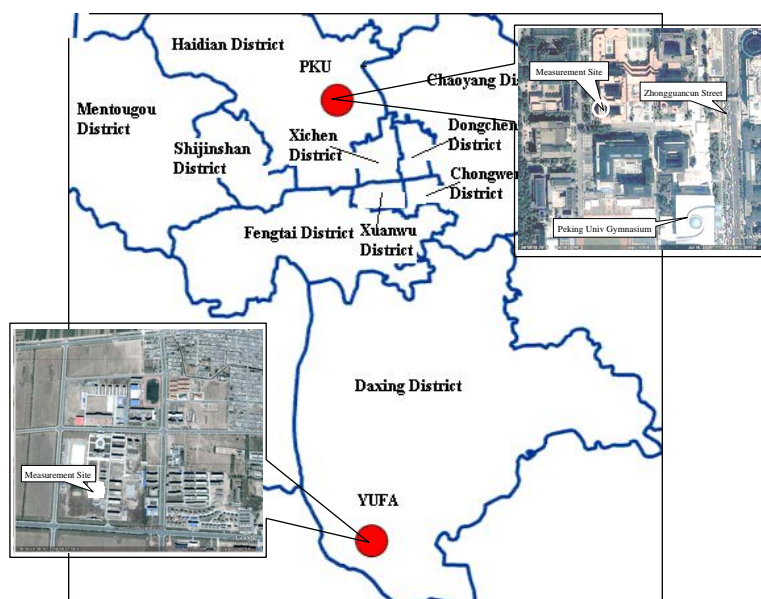
Fig. 1. Geographical locations of the sampling sites in Beijing.
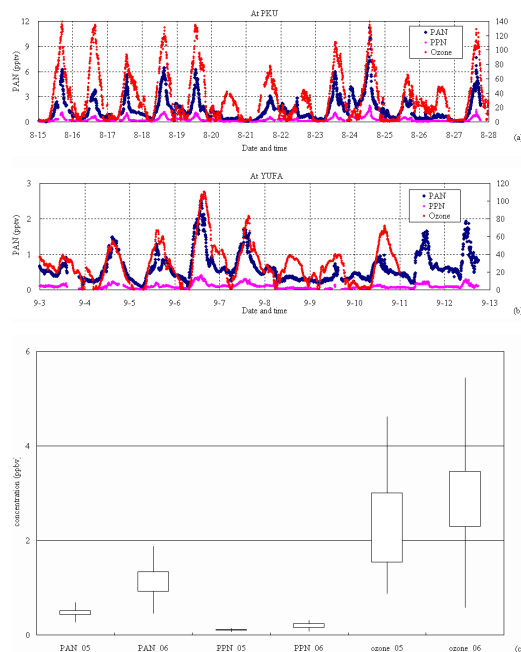
Fig. 2. Time series and inter-annual comparisons of PAN, PPN, and ozone. In order to display all information **(c)**, only one-tenth of the O_3 mixing ratios were plotted. Measurements of PAN and PPN were also taken in the summer of 2005 between 15 and 29 August. Details can be obtained from Wang and Zhang (2007). In **(c)**, the higher vertical bar represents the 3rd quartile, and the lower vertical bar represents the 1st quartile. The upper edge of the box indicates the average, and the lower edge of box indicates the median.

(a)   (b)

(c)   (d)
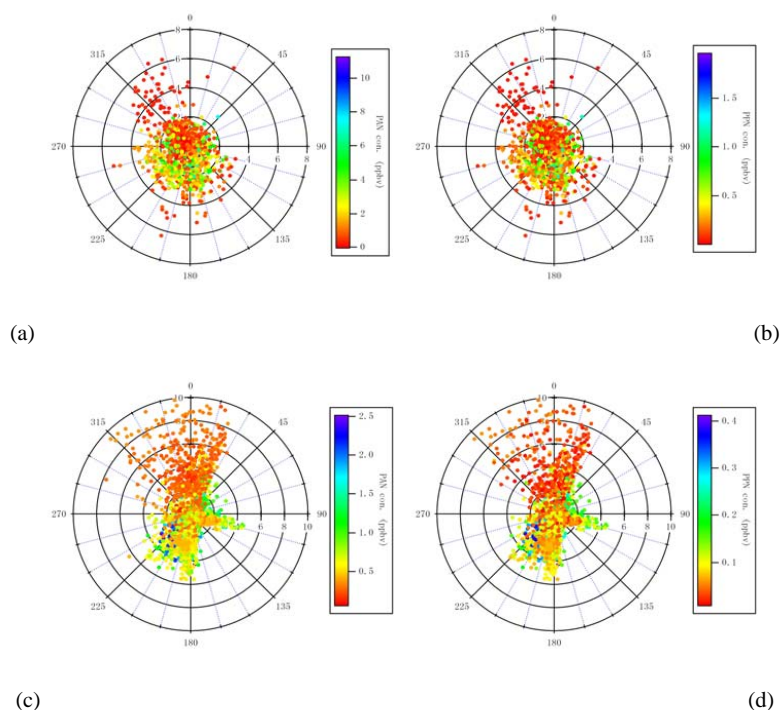
Fig. 3. Wind roses for PAN and PPN pollution Notes: At Yufa, the meteorological data was taken up to 10 September; therefore the values of PAN and PPN plotted in **(c)** and **(d)** were also consistent with the wind data input.
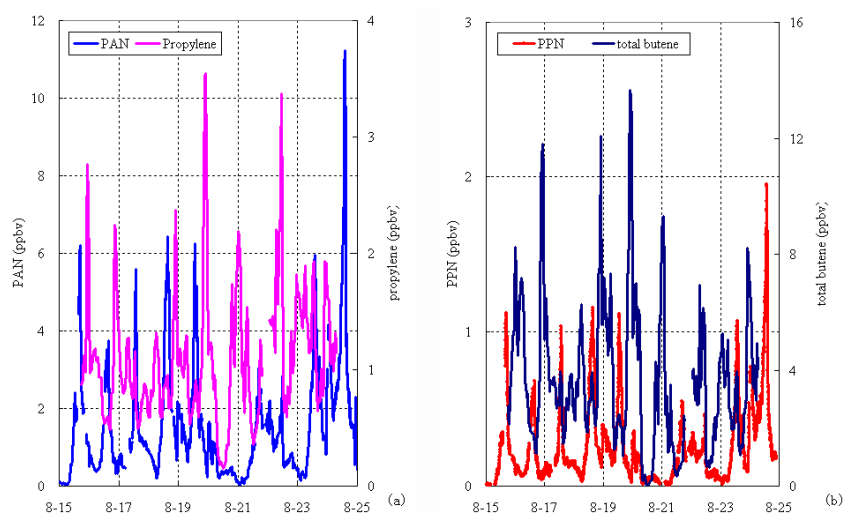
Fig. 4. PAN and PPN with their major VOC precursors at PKU Site. Butane includes n-butane, trans-2-butene, 1-butene, and cis-2-butene.
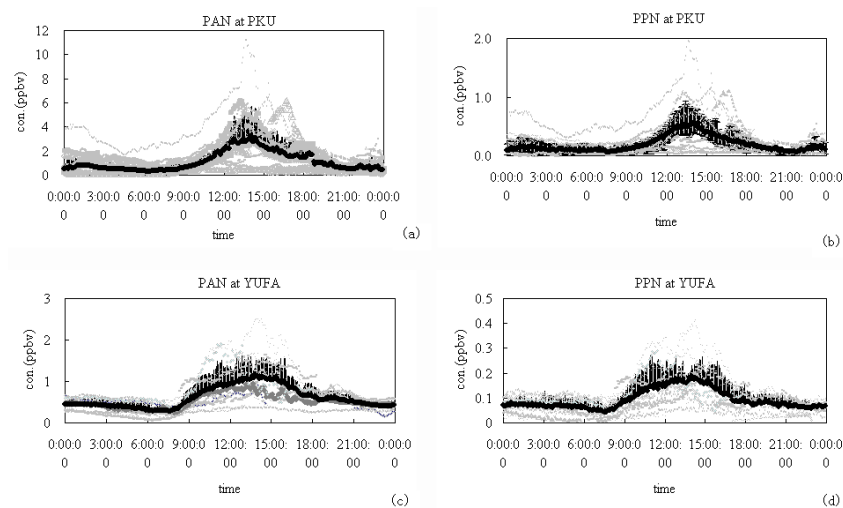
Fig. 5. Diurnal variations in PAN and PPN. Bold black lines show the median at the same time on all measurement days. Upper and lower error bars are 3rd quartile and 1st quartile, respectively.

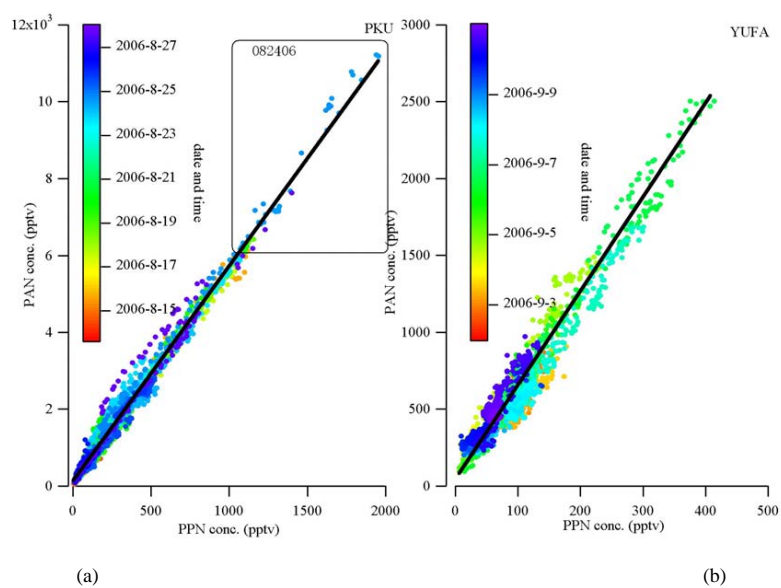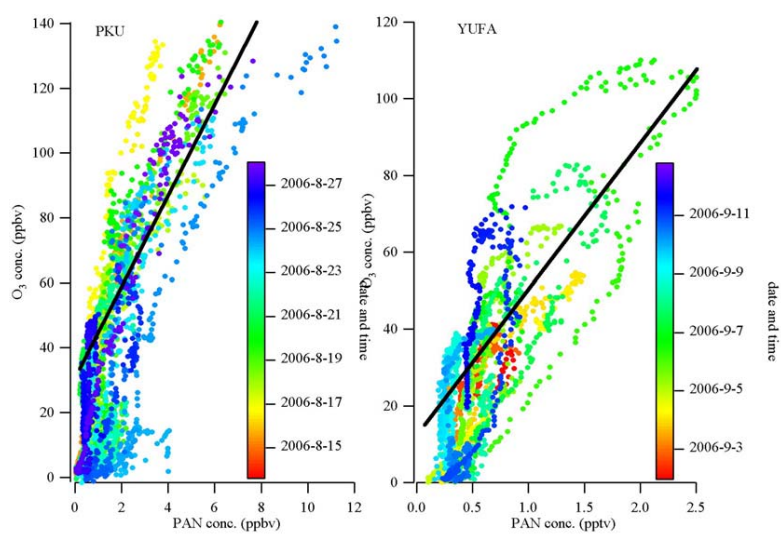**Fig. 6.** Correlation between PAN and PPN.

Fig. 7. Correlation between PAN and ozone.

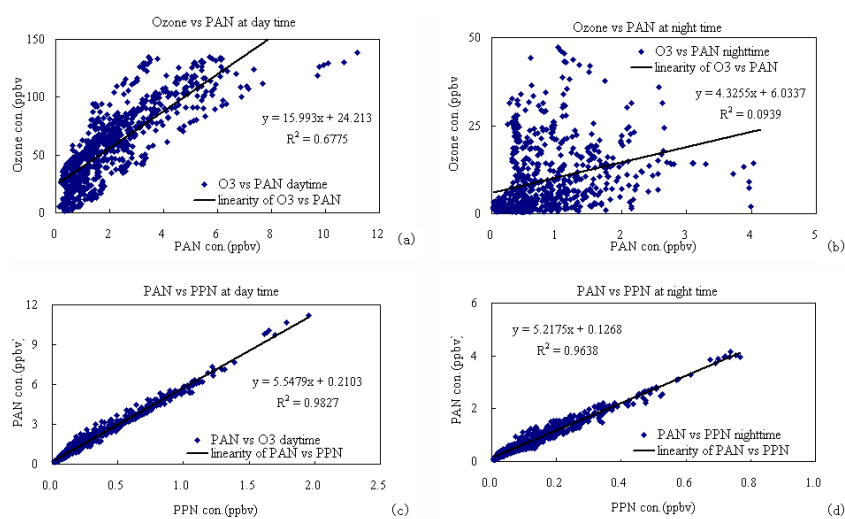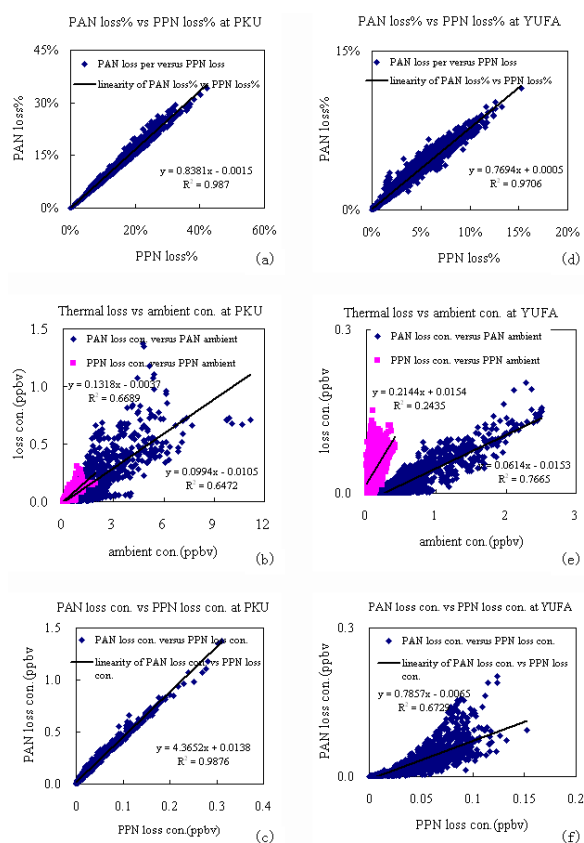**Fig. 8.** Correlations among PAN, PPN, and O$_3$.

Fig. 9. Thermal decomposition of PAN and PPN.