Summertime distributions of peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN) in Beijing: Understanding the sources and major sink of PAN

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HIGHLIGHTS

- Atmospheric PANs were measured by using GC-ECD during summertime in Beijing.
- High pollution levels of PAN and PPN were found.
- Acetaldehyde was the predominant precursor of PAN in the investigating period.
- Thermal decomposition of PAN played an important role in its chemical process.

GRAPHICAL ABSTRACT

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ABSTRACT

Peroxyacetyl nitrate (PAN), a major secondary pollutant in the atmosphere, has received much concern for its particular importance in atmospheric chemistry and adverse effects on human and plants. Atmospheric PAN and PPN were measured by using a gas chromatograph equipped with electron capture detector (GC-ECD) from June to September 2010, and the source and major sink for PAN were firstly studied in Beijing. The distinct diurnal variations of PAN and PPN with maximum in the afternoon were observed, and the mean and maximum values were 2.61 ± 2.57 ppbv ($N = 839$) and 12.5 ppbv for PAN and 0.52 ± 0.38 ppbv ($N = 152$) and 2.16 ppbv for PPN during the measuring period, respectively. Good correlation ($R = 0.85$) between PAN and PPN with a slope ($\Delta\text{PPN}/\Delta\text{PAN}$) of 0.134 indicated that anthropogenic volatile organic compounds (AVOCs) dominated the photochemical formation of PANs in Beijing. Further, we found acetaldehyde was the predominant carbonyl precursor of PAN with the contribution of 59.7% to the total peroxyacetyl (PA) radical. Methyl glyoxal, methacrolein, acetone, methyl vinyl ketone, and biacetyl contributed 7.1%, 8.8%, 19.7%, 3.4%, and 1.3% to total PA radical, respectively. Anti-correlation between PAN concentrations and the NO/NO₂ ratios was found during the whole investigating period. In addition, the amount of PAN lost by thermal decomposition (TPAN) accounted for remarkable fractions of PAN observed under high temperature during both daytime and nighttime.

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1. Introduction

Peroxyacetyl nitrate (PAN) and its homolog compounds (hereafter related to PANs, RC(O)OONO_2) are typically produced from photochemical processes involving nitrogen oxides (NO_x , NO and NO_2) and volatile organic compounds (VOCs) (Aikin et al., 1982; Lonneman et al., 1976; Singh and Hanst, 1981). PANs are thermally unstable in the lower troposphere, but are quite stable in the upper troposphere and can be transported over long distances from the polluted continental regions into the remote troposphere (Honrath et al., 1996). The release of NO_2 from the thermal decomposition of PANs has been considered as an important NO_x source for remote troposphere where they may contribute to the photochemical production of O_3 (Singh, 1987). Additionally, PANs have been recognized as lachrymators (Altshuler, 1978), mutagens (Shepson et al., 1986), and phytotoxins (Taylor, 1969). Although the atmospheric concentration of PANs in polluted areas is usually about one magnitude lower than that of O_3 , the phytotoxic effect of PANs is about 1–2 magnitude greater than that of O_3 .

PAN, the most abundant species among PANs, has been extensively measured in various regions since the first recognition of PAN in a photochemical smog (Stephens et al., 1956). The mixing ratios of atmospheric PAN range from tens pptv (parts per trillion by volume) in remote areas (Bottenheim and Gallant, 1989; Moore and Remedios, 2010; Singh and Salas, 1983) to several ppbv (parts per billion by volume) in cities (Duane et al., 2002; Grosjean et al., 2002; Lee et al., 2008; McFadyen and Cape, 2005). In China, photochemical pollution has gradually provoked much concern with extensive studies of O_3 and VOCs (Shao et al., 2006, 2009; Wang et al., 2003, 2006; Xu et al., 2008). However, the published researches related to PANs in rural and urban atmosphere of China are relatively sparse, and a few groups implemented sporadic observations (Liu et al., 2010; Wang et al., 2010; Wang and Zhang, 2007; Yang et al., 2009; Zhang and Tang, 1994). In the megacity of Beijing, only few PAN measurements have been conducted in summertime, and the remarkably high levels of PAN (up to 14 ppbv) observed surpass those measured over other urban regions in recent years (Liu et al., 2010; Wang and Zhang, 2007). However, previous studies only focused on PAN's concentration levels and diurnal variations, its source and major sink were not clearly understood. To the best of our knowledge, only Liu et al. (2010) employed a 1-D version of a chemical transport model to study the dominant source for atmospheric PAN in Beijing (Liu et al., 2010).

In this study, atmospheric PAN and PPN were measured from June to September 2010 in Beijing. In terms of the source of PAN, we discussed the relationships among PAN, PPN, and NO_x and further estimated the peroxyacetyl (PA) radical production from acetaldehyde, acetone, methacrolein (MACR), biacetyl, methyl glyoxal (MGLY), and methyl vinyl ketone (MVK), respectively. In addition, the PAN lost by thermal decomposition (TPAN) for clear days chosen from each month was calculated to investigate its thermal decomposition as major sink in the atmospheric chemical process of PAN.

2. Experimental

2.1. Site description

In this study, field sampling was conducted on the sixth floor of the Environmental Technological building (20 m above the ground level) in the Research Center for Eco-Environmental Sciences (RCEES), which is located in the north of Beijing city (39.8°N, 116.5°E) between the 4th and 5th ring roads. The surroundings of RCEES are several institutes, campuses, residential apartments, and

two side roads with moderate traffic.

2.2. Experimental methods

The detail information about PAN measurement and calibration were described in our previous study and summarized briefly here (Zhang et al., 2012a,b). Ambient air was sampled into the GC loop (0.5 mL) by a mini-pump (NMP830KNDC, KNF Inc.) via a Teflon tube (3 mm OD, 6 m length) with a flow rate of $\sim 1.5 \text{ L min}^{-1}$. Each sampling time was 20 s and the pressure was equilibrated for 5 s with the pump power off, and then the air sample was injected into GC-ECD via a six-port valve. Capillary column of DB-1 (30 m length, 0.32 mm ID, 1.0 μm film thickness) was adopted as separation column. The temperatures of the separation column and the ECD were set to be 20 °C and 38 °C, respectively. The detection limits (three times the signal to noise) of PAN and PPN were 22 and 36 pptv, respectively. The calibration of instrument for PAN was achieved by Model 42i NO_x analyzer (Thermo Scientific, USA), according to the in-situ formation of PAN via photochemical reaction of a gaseous mixture of excess acetone with NO in a 10 L Teflon bag under irradiation of 254 nm low-pressure mercury lamps. NO could be completely converted to PAN in presence of excess acetone after 5 min irradiation. Then the formed PAN concentration in the gaseous mixture was quantified by NO_x analyzer and simultaneously detected by GC-ECD. The overall uncertainty for measuring atmospheric PAN was estimated to be $\pm 15\%$ based on the combined uncertainties of the GC precision and the uncertainties of NO_x calibration system. The calibration was conducted every two days and the results showed no significant drift within one week. Atmospheric O_3 and NO_x were measured using ozone analyzer (Model 49i, Thermo Scientific) and NO_x analyzer (Model 42i, Thermo Scientific), respectively. The sampling frequency was half hour or 1 h, mostly conducting from 09:00 am to 21:00 pm (LT, Beijing time). The sampling days were randomly selected for 7 days in June, 13 days in July, 7 days in August, and 9 days in September.

The VOCs measurements including acetaldehyde, acetone, MVK, and MACR were also concurrently conducted by our group from June to August 2010 at this sampling site (Zhang et al., 2012a,b, 2014). The analysis procedure was mainly based on the EPA TO-11A method (EPA, 1999), and the details have been described in our previous publications (Pang and Mu, 2006). Carbonyls were sampled at least 4 days per month, with carbonyls' samples collected at 2 h interval.

3. Results and discussion

3.1. Ambient concentrations of PAN and PPN

PAN could be detected in nearly all samples during the whole period, whereas PPN was frequently below the detection limit of the GC-ECD except August. In June 2010, we stopped the integrator after the elution of the PAN peak due to without the calibration of PPN, so no PPN measurements are available for this period.

Fig. 1 shows the time series of the mixing ratios of ambient PAN and PPN. During the investigating period the mean and maximum values were 2.61 ± 2.57 ppbv ($N = 839$) and 12.5 ppbv for PAN and 0.52 ± 0.38 ppbv ($N = 152$) and 2.16 ppbv for PPN, respectively. Apparently, the concentrations of PAN in July were much lower in comparison with other months, which were possibly ascribed to the extremely synoptic situation. During July there were sixteen rainy days, six clear days with extremely high temperature ($T > 37^\circ\text{C}$). For these clear days in July, the average temperature was up to 32°C , higher than 28°C in June, 29°C in August, and 26°C in September. It's well known that the rainy days often represent weak photochemical reactivity which limits PAN

Fig. 1. Time series of ambient PAN and PPN in Beijing during Jun.–Sep., 2010.

formation, and the extremely high air temperature during the clear days greatly accelerated PAN thermal decomposition as discussed in the Section 3.5. In addition, O_3 and NO_x were both found to be generally lower in July than other months. It was ascribed to the weak atmospheric photochemical activity which inhibits the formation of O_3 and the significant effect of wet deposition on the removal of NO_x during the continuous rainy days in July, respectively. But for the primary pollution of CO, it was higher in July than other months probably due to the weak diffusion under the stable synoptic condition.

The mean diurnal profiles of PAN and PPN measured by this study in August are illustrated in Fig. 2 for comparison with other studies. The mean daily maximum PAN concentration of 5.5 ppbv observed in this study was in good agreement with the value (5 ppbv) reported by Liu et al. (2010) in August 2007. Compared with other studies in Beijing, the maximum PAN value (7.0 ppbv) observed by this study was higher than 2.5 ppbv observed in August 2005 (Wang and Zhang, 2007), but lower than 11.2 ppbv in

August 2006 (Yang et al., 2009) and 14.0 ppbv in August 2007 (Liu et al., 2010). It's possibly ascribed to the interannual differences of the PAN precursors and the synoptic situation in Beijing.

It is interesting to note that evident elevation of PAN concentration after sunset (around 20:00) was frequently observed (Figs. 2 and 3), even PAN maximum appearing after sunset on 6 September (Fig. 3). The elevation of PAN after sunset was coincident with the increases of CO and NO_x which were mainly from the primary emission of vehicles. There were no evidences that PAN could be directly emitted from exhaust of vehicles, e.g., no elevation of PAN was observed when CO and NO_x significantly increased during early morning hours. The elevation of PAN concentration after sunset in Beijing was also observed by Wang and Zhang (2007) and they concluded the elevation was due to long distance transportation. Considering the similar sources and sinks for PAN and O_3 (for example, good correlation ($R = 0.76$, $N = 69$) between PAN and O_3 was found in September), if long distance transportation made contribution to the PAN elevation, O_3 would have the similar behavior. However, steady decrease of O_3 after sunset was

Fig. 2. The average diurnal variations of PAN and PPN in August 2010.

Fig. 3. The diurnal variations of PAN, NO_x , CO, and O_3 on typical clear days of 5 and 6 September.

observed. Thus we speculated that dark reactions or other sources might contribute to the elevated PAN based on the fact that photochemical reactions ceased after sunset. The special diurnal variations of PAN and O_3 on 6 September provided some clues for disclosing the reason for PAN elevation after sunset. On 6 September PAN and O_3 both exhibited evident difference from other typical clear days, e.g., instead of quick decrease of PAN after around 15:00 for most typical clear days, PAN concentration on 6 September continually increased from 8:00 to 21:00; high O_3 concentration after its maximum on the day lasted much longer time than those on most typical clear days. On 6 September the elevated PAN after sunset was negative correlated ($R = -0.83$) with the decreased O_3 (consumed by NO and/or combined with NO_2): $[PAN] \text{ ppb} = (-0.06 \pm 0.03) * [O_3] \text{ ppb} + (14.6 \pm 1.90) \text{ ppb}$. We inferred that the much higher O_3 concentration from later afternoon to sunset (around 20:00) on 6 September than those on most other clear days would facilitate conversion of NO to NO_2 and hence greatly restrain PAN thermal decomposition rate (Grosjean et al., 2001). On the other hand, the combination of O_3 and NO_2 both with the relative high concentrations just after sunset possibly favored the formation of NO_3 radicals which would accumulate due to no photolysis. NO_3 is reactive species towards various VOCs, and has been considered as the dominant species triggering nighttime atmospheric chemistry, resulting in formation of various organic radicals including peroxyacetyl (PA) radical which reacts with NO_2 to form PAN. The significant amount of PAN thermal decomposition after sunset would also make great contribution to OH radical which further initiates VOCs oxidation to partially compensate PAN thermal loss and CH_3 radical which leads to formaldehyde in turn. It's well confirmed by the findings of Duane et al. (2002) that isoprene, methacrolein (MACR), methyl glyoxal (MGLY), and methyl vinyl ketone (MVK) both reached their respective peak after sunset (ca. 20:00) accompanying with high concentration of formaldehyde in summer in Insubria, Northern Italy. In addition, inferring from the results of model simulation, Liu et al. (2010) expected that large gradient of PAN vertical distribution might exist in Beijing, the downward transport of PAN produced aloft in the boundary layer was also suspected to make great contribution to the evident elevation of PAN after sunset.

3.2. Relationship between PAN and PPN

PAN and PPN are expected to be highly correlated due to their similar photochemical process in the atmosphere (Singh, 1987). In this study, good correlation ($R = 0.85$, $N = 152$, $p < 0.0001$) between PAN and concurrently detectable PPN was found: $PPN [\text{ppbv}] = (0.134 \pm 0.007) * PAN [\text{ppbv}] + (0.027 \pm 0.029) [\text{ppbv}]$. However, their precursors are not identical. The precursors of PAN, leading to the peroxyacetyl (PA) radical, come from both human activity and biogenic emissions, while the precursors of PPN, leading to the peroxypropionyl radical, are predominantly anthropogenic in origin (Grosjean et al., 2001; Roberts et al., 2004). Thus, the ratio of PPN to PAN provides an indicator to evaluate the relative importance of anthropogenic and biogenic VOCs in PANs formation. With extensive measurements, Roberts et al. (2002, 2004) concluded that the formation of PANs was dominated by anthropogenic sources when the slope ($\Delta PPN/\Delta PAN$) was between 13.5% and 17.2% and was dominated by biogenic sources when the slope was less than 10% (Roberts et al., 2004, 2002). The slope of 13.4% reported here, which was comparable with the reported values of 0.135–0.172 in polluted urban areas (Roberts et al., 2002, 2004), indicated that anthropogenic VOCs (AVOCs) were dominating the photochemical production of PANs during summer in Beijing.

3.3. Relationship between PAN and NO_x

As shown in the reaction Equations R1–R3, PAN formation depends on complex atmospheric chemical reactions of VOCs and NO_x , and the thermal decomposition rate of PAN depends on the ratio of NO to NO_2 (NO/NO_2) in addition to air temperature. Therefore, atmospheric PAN concentration was correlated with NO_x concentration and the NO/NO_2 ratio. Owing to the same responds of PAN and NO_2 on the analyzer (Gerboles et al., 2003; Zhang et al., 2012a,b), we defined NO'_2 and NO'_x representing the actual concentrations of NO_2 and NO_x after subtracting PAN concentration from the NO_2 and NO_x values displayed in the NO_x analyzer, respectively. Very weak positive correlation ($R = 0.07$, $N = 537$, $P = 0.101$) between PAN and NO'_x was found during our investigated period, which was in contrast with the result observed in clean marine air of the Pacific where PAN concentration was found to increase with increasing NO_x (Singh et al., 1985). In the remote areas, NO_x mostly presents as NO_2 , whereas in the polluted city of Beijing, large amount NO emission from vehicles would greatly favor PAN thermal decomposition, leading to the weak correlation. Fig. 4 showed PAN concentrations as a function of NO/NO'_2 in Beijing. Apparently, almost no high PAN concentrations appeared at high NO/NO'_2 ratios, further confirming that NO favors PAN thermal decomposition. The relationship between PAN and NO/NO'_2 ratio obtained by this study was in good agreement with previous studies in other cities (McFadyen and Cape, 2005; Schrimpf et al., 1998).

3.4. Sources of atmospheric PAN

To the best of our knowledge, two types of estimation method have been implied to investigate the sources of atmospheric PAN: the first one is based on estimating the formation potentials of

Fig. 4. PAN concentrations in Beijing as a function of NO/NO'_2 .

various hydrocarbons to PAN formation using Master Chemical Mechanism (MCM) model (Altshuller, 1993) and SAPRC 97 model (Grosjean et al., 2002), the second is recently confined to estimate the direct contribution of acetaldehyde, biacetyl, MACR, MVK, acetone, and MGLY to PA production using steady-state model (Cleary et al., 2007; LaFranchi et al., 2009). Specifically for the second estimation, PAN formation occurs upon the production of PA radical derived from the oxidation or the photolysis of acetaldehyde, acetone, MGLY, MACR, MVK, and biacetyl ($\text{CH}_3\text{COCOCH}_3$) (Altshuller, 1993). The dominant pathways leading to PA radical from the six carbonyls in the troposphere are summarized in Fig. 5 (LaFranchi et al., 2009).

In this study, based on the fact that its lifetime is very short ($\tau \sim 10$ s) relative to oVOCs ($\tau \sim 1\text{--}2$ h) (LaFranchi et al., 2009), we likewise considered PA radical in steady-state and partly followed the method simplified by LaFranchi et al. (2009) to roughly estimate the direct contributions of six compounds to PA production. Atmospheric PAN formation is determined by the formation rates of PA radicals which depend on the concentrations of the carbonyls and OH radicals, the rate constants of their reactions with OH or photolysis, and the branching ratios of the reactions for formation of PA radicals. The average concentrations of the carbonyls, the rate constants of OH reactions and photolysis, and the branch ratios of PA formation adopted in this study are summarized in Table 1. Note that during the investigating period, the data of acetaldehyde and acetone were detected in all samples ($N = 69$) with average concentrations of 4.93 and 11.1 ppbv, the MACR (co-elute with butanal)

data were often obtained with the average concentration of 0.84 ppbv. MVK was sometimes below detection limit and averaged to 0.30 ppbv with limited data ($N = 21$). MGLY was estimated to be 0.47 ppbv according to the observed ratio (0.62) of MVK to MGLY (Shao et al., 2009). To date, biacetyl has not been measured in Beijing. In this study we roughly estimated biacetyl concentration as 0.09 ppbv approximately as that of glyoxal which was inferred from the reported ratio of 0.32 of glyoxal to MVK in the summer of Beijing (Shao et al., 2009).

The PA formation rates estimated for the six carbonyls as well as their proportion to the total are shown in Fig. 6. It is evident that acetaldehyde is the dominant source for PA formation with the contribution of 59.7% among the six carbonyls in Beijing, which was in agreement with the conclusion that acetaldehyde is often the dominant PA radical source over urban areas (Kondo et al., 2008; Roberts et al., 2001). The photolysis of acetone is the second largest contribution to the total PA radical with the production rate of ca. 3.0×10^6 molecules $\text{cm}^{-3} \text{s}^{-1}$. MACR and MGLY contributed to the formation of PA radical with the rate of ca. 1.35×10^6 molecules $\text{cm}^{-3} \text{s}^{-1}$ and 1.09×10^6 molecules $\text{cm}^{-3} \text{s}^{-1}$, respectively. Although the photolysis rate of biacetyl is as fast as $4.4 \times 10^{-5} \text{s}^{-1}$, its contribution to the PA radical is very small due to its very low concentration in the atmosphere. In this study, considering the combination of systematic and random errors, we estimated the uncertainty ($\sim 15\%$) as much as a factor of 3 relative standard deviation in detecting these carbonyls (Pang and Mu, 2006), and calculated individual variations of acetaldehyde (17.91%), acetone

Fig. 5. Mechanism for the production of peroxyacetyl (PA) radical.

Table 1

Summary of the reactions for the production of PA radical with the observed and inferred concentrations and the rate constants used in the analysis.

Carbonyls	Concentrations (ppbv)	Rate constants with OH ^c (molecules cm ⁻³ s ⁻¹)	α^{OH}	Photolysis rates (s ⁻¹) ^f	$\alpha^{\text{photolysis}}$
Acetaldehyde	4.93 ^a	$1.5 \times 10^{-11\text{d}}$	1	0.5×10^{-5}	–
MGLY	0.47 ^b	$1.5 \times 10^{-11\text{d}}$	1	1.9×10^{-5}	1
MACR	0.84 ^a	$2.9 \times 10^{-11\text{d}}$	0.45	0.2×10^{-5}	–
MVK	0.30 ^a	$2.0 \times 10^{-11\text{d}}$	0.7	2.2×10^{-5}	–
Acetone	11.1 ^a	$1.8 \times 10^{-13\text{d}}$	–	1.1×10^{-5}	1
Biacetyl	0.09 ^b	$2.4 \times 10^{-13\text{e}}$	–	4.4×10^{-5}	2

 α^{OH} and $\alpha^{\text{photolysis}}$ are the branching ratios for PA radical formation via the reaction with OH radical and the photolysis, respectively (Atkinson et al., 2006).^a Data cited our previous work (Zhang et al., 2012a,b, 2014).^b Data inferred from (Shao et al., 2009).^c OH concentration was assumed to be constant and estimated to be 5×10^6 molecules cm⁻³ during summertime in Beijing (Liu et al., 2012).^d Recommended by Atkinson et al. (2006) at 298 K.^e Recommended by Darnall et al. (1979).^f The maximum photolysis rates were calculated at noon on 12 August in Beijing based on the actinic fluxes (Finlayson-Pitts and Pitts, 1986) and the absorption cross sections of acetaldehyde (Martinez et al., 1992), MGLY (Meller et al., 1991), MACR (Gierczak et al., 1997), MVK (Gierczak et al., 1997), acetone (Meyrahn et al., 1986), and biacetyl (Horowitz et al., 2001).

(5.91%), MACR (2.64%), MGLY (2.13%), MVK (1.02%), and biacetyl (0.39%) in the total PA production rate. Therefore, the total uncertainty was estimated to be ~30% by summing individual variations above in this study.

3.5. Major sink of PAN: thermal decomposition

Laboratory investigations have indicated that thermal decomposition is the predominant removal pathway of PAN in the daytime (Roberts and Bertman, 1992; Senum et al., 1986; Grosjean et al., 2001), because its reaction rate with OH radical (Wallington et al., 1984) and its photolysis are slow (Senum et al., 1984) as well as the low wet deposition rate (Gaffney et al., 1987). From the reactions (R2, R-2, and R3) illustrated in Section 3.3, the PAN lost by thermal decomposition (TPAN) is given by Equation (1).

$$-\text{dln}[\text{PAN}]/\text{dt} = k_{-2}k_3[\text{NO}]/(k_3[\text{NO}] + k_2[\text{NO}_2']) \quad (1)$$

k_{-2} and k_3 are the reaction rate constants for reactions R-2 and R3, respectively. [PAN], [NO], and [NO₂'] represent the concentrations. k_3/k_2 of 1.95 ± 0.28 has been found to be independent of temperature from 10 °C to 40 °C under standard atmospheric

pressure (Tuazon et al., 1991), and thus the Equation (1) could be simplified as Equation (2) by replacing k_3 with k_{-2} .

$$-\text{dln}[\text{PAN}]/\text{dt} = k_{-2}/(1 + [\text{NO}_2']/1.95[\text{NO}]) \quad (2)$$

Because the rate constant k_{-2} is temperature dependent, $k_{-2}(\text{s}^{-1}) = 2.52 \times 10^{16} e^{(-13,573/T)}$ (Tuazon et al., 1991), the thermal decomposition rate of atmospheric PAN depends both on temperature and the ratio of [NO₂']/[NO]. The amount of PAN lost by thermal decomposition (designated as TPAN) could be integrated over 1 h from the measured PAN concentration and the decomposition rate of PAN derived from Equation (2) at each temperature and the [NO₂']/[NO] ratio encountered during field measurement. Positive correlation (Slope{[(TPAN/PAN)/T]} = 0.080 ± 0.006 , Intercept = -23.7 ± 1.92 , R = 0.95, SD = 0.176, P < 0.0001) between TPAN/PAN and air temperature (T) was found in the temperature range of 293–313 K in this study. Fig. 7 illustrates the diurnal variations of TPAN and PAN on 24 June, 5 July, 12 August, and 4 September as the typical clear days in each month. As clearly seen in Fig. 7B, TPAN greatly exceeded the observed PAN from morning to late afternoon owing to the extremely high air temperatures (above 35 °C) throughout the day. The relatively high TPAN, the abnormal trend (PAN concentrations decreased from morning to noontime), and the extremely low values of PAN (less than 0.6 ppbv) on the day in July indicated that the newly formed PAN via photochemical reactions might be totally consumed by the thermal decomposition. Because the air temperature on the days in June, August, and September in the morning (all lower than 30 °C) was much less than that on the day in July, the TPAN accounted for smaller fraction of the total (PAN + TPAN) than that on the day in July, and accumulation of atmospheric PAN formed via photochemical reactions from morning to afternoon was observed. In the late afternoon, photochemical reactivity decreased (mainly due to decrease of OH radicals), while thermal decomposition of PAN still kept high rate, atmospheric PAN decreased accordingly. Although the photochemical reactivity (implying PAN formation potential) in September became much less than that during summertime (from June to August), the peak values of PAN observed in September were comparable to (or even greater than) those observed in June and August (Fig. 7). The TPAN in each hour (with only the exception on 16:00) on the day in September was lower than PAN (Fig. 7D), whereas the TPAN after noontime in the summer months was always greater than PAN (Fig. 7A–C). It is evident that the relatively high PAN peak values observed in September were

Fig. 6. The PA production rate for each source and their respective contributions.

Fig. 7. The diurnal variations of observed PAN and calculated TPAN on 24 June (A), 5 July (B), 12 August (C), and 4 September (D).

reasonably ascribed to the remarkable decrease of PAN consumed by thermal decomposition.

4. Conclusion

In our study, high pollution level of PAN and PPN were observed in Beijing during summertime. The results of correlation analysis between PAN and PPN indicated that AVOCs dominated the photochemical formation of PANs in Beijing. Further, acetaldehyde was found to be the predominant precursor of PAN with the contribution of 59.7% to the total peroxyacetyl (PA) radical. As expected, the amount of PAN lost by thermal decomposition (TPAN) accounted for remarkable fractions of PAN observed under high temperature during both daytime and nighttime.

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