Seasonal and diurnal variations of atmospheric peroxyacetyl nitrate, peroxypropionyl nitrate, and carbon tetrachloride in Beijing

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Abstract
Atmospheric peroxyacetyl nitrate (PAN), peroxypropionyl nitrate (PPN), and carbon tetrachloride (CCl4) were measured from September 2010 to August 2011 in Beijing. PAN exhibited low values from mid-autumn to early spring (October to March) with monthly average concentrations ranging from 0.28 to 0.73 ppbV, and increased from early spring to summer (March to August), ranging from 1.37–3.79 ppbV. The monthly variation of PPN was similar to PAN, with low values (below detection limit to 0.18 ppbV) from mid-autumn to early spring, and a monthly maximum in September (1.14 ppbV). The monthly variation of CCl4 was tightly related to the variation of temperature, exhibiting a minimum in winter (69.3 pptV) and a maximum of 180.6 pptV in summer. Due to weak solar intensity and short duration, PAN and O3 showed no distinct diurnal patterns from morning to night during winter, whereas for other seasons, they both exhibited maximal values in the late afternoon (ca. 15:00 to 16:00 local time) and minimal values during early morning and midnight. Good linear correlations between PAN and PPN were found in autumn ($R^2=0.91$), spring ($R^2=0.94$), and summer ($R^2=0.81$), with slopes of 0.130, 0.222, and 0.133, respectively, suggesting that anthropogenic hydrocarbons dominated the photochemical formation of PANs in Beijing. Positive correlation between PAN and O3 in summer with the low slopes ($\Delta$O3/$\Delta$PAN) ranging from 9.92 to 18.0 indicated serious air pollution in Beijing, and strong negative correlation in winter reflected strong O3 consumption by NO titration and less thermal decomposition of PAN.

Introduction
Peroxyacetyl nitrate (PAN), peroxypropionyl nitrate (PPN), and other homologue compounds (thereafter related to PANs, RC(O)OONO2) are crucial components of the odd-nitrogen compounds (NOy) in the atmosphere and particularly important secondary pollutants formed via photochemical reactions of volatile organic compounds (VOCs) in the presence of NOx (Aikin et al., 1982; Singh, 1987; Singh and Hanst, 1981). PANs play important roles in atmospheric chemistry and have adverse impacts on human health and ecosystems. PAN, as the most abundant species among PANs, has been recognized as lachrymators (Altshuller, 1978), mutagens (Shepson et al., 1986), and phytotoxins (Sun and Huang, 1995; Taylor, 1969). PPN as the second largest species among PANs, its atmospheric concentration usually accounts for 4%–20% of PAN (Grosjean et al., 2001, 2002; Lee et al., 2008; Zhang et al., 2011), and it is four times phytotoxic (Kleindienst et al., 1990) and five times eye-irritant than that of PAN (Altshuller, 1978). Furthermore, PAN and some of its analogues have been found to 10–50 times toxic than that of O3 (Gaffney and Marley, 2001a, 2001b; Taylor, 1969). Atmospheric PAN is exclusively from tropospheric photochemical reactions, and hence, PAN has been considered as a better indicator of photochemical smog pollution than O3 (McFadyen and Cape, 2005). PANs are thermal unstable compounds, they are quite stable in the mid and upper troposphere under low temperature, and can be
transported over long distances from polluted continental regions into the remote areas where they release NOx under high temperature (Honrath et al., 1996; Kondo et al., 1997; Singh et al., 1996), and hence PANs act as important temporary NOx reservoirs and control the photochemical production of O3 in the remote troposphere (Singh and Hanst, 1981). Due to the particular importance of PANs on atmospheric chemistry, a great number of PANs measurements have been conducted intensively in developed countries, including the urban regions (Grosjean et al., 2001; Marley et al., 2007; Roberts et al., 1995) and remote area (Hartsell et al., 1994; Roberts et al., 2004; Singh et al., 1990, 1992; Williams and Grosjean, 1991). However, only few researches involving with PANs are implemented in developing countries of Asia (Lee et al., 2008; Watanabe et al., 1998; Zhang and Tang, 1994; Wang et al., 2010; Zhang et al., 2009).

Carbon tetrachloride (CCl4), another species investigated in this work, is widely used in the synthesis of chlororulluorocarbons and as a solvent in the past chemical processes (Altshuller, 1976). CCl4 is chemical inert in the troposphere, difficult to photolysis and non-reactive towards the tropospheric oxidants (Cox et al., 1976). Therefore, the emitted CCl4 can ultimately diffuse into the stratosphere where it will release chlorine atoms under the intensive ultraviolet sunlight irradiation and participate in stratospheric ozone depletion (Molina and Rowland, 1974). To date, numerous global observation networks have been established for CCl4 in the developed countries (Derwent et al., 1998; Happell and Roche, 2003; Lovelock et al., 1973; Simmonds et al., 1988), but very limited measurements in China (Barletta et al., 2006; Sun et al., 2010; Yao et al., 2010).

Beijing, the capital of China, is suffering from serious photo-oxidants pollution as indicated by elevation of O3 (Gao and Zhang, 2012; Shao et al., 2009; Tang et al., 2009; Wang et al., 2006; Zhang et al., 2004). However, the measurements of PANs as the indicator of photochemical pollution, in the megacity are relatively sparse (Wang and Zhang, 2007; Yang et al., 2009; Zhang et al., 2011), and the existing studies mostly carried out over short period during summer, generally a few weeks.

In this study, we conducted measurements of atmospheric PAN, PPN, CCl4, and O3 from September 2010 to August 2011 in Beijing, and elucidated the seasonal and diurnal variations of PAN, O3, and CCl4.

### 1 Experimental

#### 1.1 Site description

Field measurements were 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 (40.0° N, 116.3° E). The surroundings of RCEES are several institutes, campuses, residential apartments, and two side roads with moderate traffic. The RCEES is moderately covered by various plants, including *P. orientalis*, *Pendula loud*, *P. simonii*, and *S. matsudana koidz.*

#### 1.2 Determination of PANs and CCl4

Atmospheric PANs and CCl4 were measured by HP-5890 gas chromatography equipped with 63Ni electron capture detector and a capillary column DB-1 (30 m length, 0.32 mm ID, Agilent Company). A Teflon tube (3 mm OD, 6 m length) with a flow rate of 1.5 L/min. Each sampling time was 20 sec and the pressure was equilibrated for 5 sec with the pump power off, and then six-port valve (MGS-4, Shimadzu, Japan) was switched for GC-ECD analysis. The analyzing frequency was set to 30 min. The instrument calibrations for PAN and PPN were carried out by evaporation of synthesized PAN and PPN solution in a Teflon bag, and the concentrations of PAN and PPN in the solutions were quantified by IC based on the quantitative conversion of PAN and PPN to NO2 under hydrolysis in sodium hydroxide solution. For calibration of CCl4, gaseous CCl4 was also obtained via the volatilization of a known amount of liquid CCl4 into 10 L Teflon bag at 50°C and followed by GC analysis. The overall uncertainties for measuring atmospheric PAN and PPN were estimated to be ±13%, and for CCl4 was approximately ±5%. The detection limits (three times the signal to noise ratio, 3 S/N) for PAN, PPN and CCl4 were estimated to be 22, 36, and 5 pptV, respectively.

#### 1.3 Determination of ambient O3 and NOx

The measurements of ambient ozone and NOx were simultaneously conducted from September 2010 to August 2011 using Model 49i ozone analyzer and Model 42i NOx analyzer (Thermo Scientific, USA), respectively. The O3 analyzer was calibrated by using Thermo Scientific Model 49i-PS ozone calibrator once every 3 months. The detection limit (3S/N) for ozone measurement was 1 ppbV, and the total measurement uncertainty was about 5%. For the calibration of NOx analyzer, it was achieved by Thermo Scientific Model 146i with NO standard gas. The detection limit (3S/N) for NOx measurement was 0.4 ppbV, and the total measurement uncertainty was estimated to be 5%.
2 Results and discussion

2.1 Monthly variations

The monthly variations of PAN, PPN, O₃, CCl₄ and Temperature are illustrated in Fig. 1. It should be mentioned that the concentrations of PPN in October, December, and January were below the detection limit of instrument (3S/N = 36 pptV), and 0.036 ppbV was used as the monthly mean PPN concentrations for these months. As shown in Fig. 1, both common and different characters among the monthly variations of the four pollutants could be seen. Because atmospheric PAN, PPN and O₃ are the secondary pollutants from photochemical reactions of VOCs and NOₓ, the sharply decrease of PAN, PPN and O₃ from September to October was ascribed to the decrease of sunlight intensity and duration (Fig. 1d). Pulse increase of PAN and PPN were observed in February, but O₃ in this month kept as constant low value as other months in winter. It should be mentioned that stagnant air condition with bad atmospheric visibility (usually called haze day) frequently occurred in February 2011, and serious accumulation of primary pollutants was observed, e.g., the daily mean concentration of NO on 23 February achieved 70.7 ppbV and of NO₂ was 84.5 ppbV. The weak sunlight under the haze days might not efficiently trigger NO₂ photolysis to form O₃ (Reactions (4)–(5)), and the titration of the high concentration of NO on O₃ (Reaction (6)) greatly suppressed O₃ concentration as well. As for PAN and PPN, their thermal decomposition rates become extremely low under the extremely low air temperature in the winter (Reactions (8)–(11)), and hence the formed PAN and PPN through the reactions of OH with VOCs could be easily accumulated under the stagnant air condition (Reactions (1), (2), and (7)).

\[
\begin{align*}
\text{RH} + \text{OH} & \rightarrow \text{R} + \text{H}_2\text{O} \\
\text{R} + \text{O}_2 & \rightarrow \text{RO}_2 \\
\text{RO}_2 + \text{NO} & \rightarrow \text{RO} + \text{NO}_2 \\
\text{NO}_2 + \text{hv} & \rightarrow \text{NO} + \text{O} \\
\text{O} + \text{O}_2 + \text{M} & \rightarrow \text{O}_3 + \text{M}
\end{align*}
\]
HONO formed from the heterogeneous reaction of NO$_2$ easily form OH radical under weak sunlight irradiation, should be negligible. Because photolysis of HONO can as well as the reactions of O$_3$ with unsaturated alkenes.

Table 1. The maximal concentrations (12.52 ppbV for PAN in September 2010, and 2.50 ppbV for PPN in May 2011) observed in this study were in the range of the reported maximal values of 2.49–17.8 ppbV for PAN and 0.5–2.48 ppbV for PPN in Beijing (Wang and Zhang, 2007; Xu et al., 2011; Yang et al., 2009). The mean CCl$_4$ concentration of (175.0 ± 70.9) pptV (except the extremely high value of 1417 pptV) in August 2011 was generally comparable with (108.0 ± 12.5) pptV observed by Sun et al. (2010) in August 2009 in Beijing and (114 ± 11) pptV reported by Barletta et al. (2006) from the measurements of 45 cities in China, but was apparently higher than the background values at the Shangdianzi Global Atmosphere Watch Station (89.4 ± 0.7) pptV) in Beijing (Yao et al., 2010). Although CCl$_4$ used as a cleaning reagent had been banned since 2007 according to the agreements of the Montreal Protocol for China, its usage as a chemical auxiliary should have been phased-out in 2010 (Zurer, 1995). In comparison with background stations, the relatively high CCl$_4$ concentration measured implied that CCl$_4$ might be still used as a chemical auxiliary in Beijing during the sampling period.

2.2 Diurnal variations

The diurnal patterns of PAN, O$_3$, and CCl$_4$ during the whole year are shown in Fig. 2. The diurnal variations of PAN in the seasons other than winter exhibited similar trends to O$_3$, namely maximal values in the late afternoon (ca. 15:00 to 16:00 local time) and minimal values during early morning and midnight. Such diurnal variation trends firstly demonstrated that PAN and O$_3$ are both secondary pollutants formed from photochemical reactions in daytime. On the other hand, NO emitted from vehicle exhaust during rush hours in the late afternoon greatly consumed PAN and O$_3$ through thermal decomposition and titration, respectively. In contrast to other seasons, the diurnal variation of PAN in winter exhibited PAN concentration gradually and slowly increased from early morning to late afternoon. Because atmospheric PAN under the low temperature in winter is very stable, the weak PAN formation through photochemical reactions would accumulate and result in the continually slow increase of PAN concentration. As for O$_3$ during winter, the fast decrease after 16:00 indicated O$_3$ titration by NO dominated O$_3$ loss.

CCl$_4$, as a primary pollutant, pulse increase of its concentration was frequently observed during the investigating days in each season, indicating pulse sources of CCl$_4$ existed nearby our sampling site, e.g. the CCl$_4$ solvent used in the laboratories in RCEES. In general, the average atmospheric CCl$_4$ concentrations in Beijing were kept nearly constant during days in each season, contrasting to the diurnal variations of other primary pollutants, such as CO and NO$_x$ with high concentrations during rush hours in early morning and later afternoon and with low values in noontime and afternoon. Both sources’ strength and dif-
Table 1  Sample number and the mean, minimum, median and maximum concentrations for PAN, PPN, O$_3$ and CCl$_4$ in each month (unit: ppbV)

<table>
<thead>
<tr>
<th>Month</th>
<th>Species</th>
<th>N</th>
<th>Mean ± SD</th>
<th>Min</th>
<th>Median</th>
<th>Max</th>
</tr>
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<tbody>
<tr>
<td>Sep</td>
<td>PAN</td>
<td>228</td>
<td>3.98 ± 2.93</td>
<td>0.20</td>
<td>3.49</td>
<td>12.52</td>
</tr>
<tr>
<td></td>
<td>PPN</td>
<td>16</td>
<td>1.14 ± 0.39</td>
<td>0.75</td>
<td>0.96</td>
<td>2.16</td>
</tr>
<tr>
<td></td>
<td>O$_3$</td>
<td>88</td>
<td>45.0 ± 25.9</td>
<td>5.13</td>
<td>42.47</td>
<td>98.00</td>
</tr>
<tr>
<td></td>
<td>CCl$_4$</td>
<td>228</td>
<td>0.078 ± 0.055</td>
<td>0.021</td>
<td>0.057</td>
<td>0.47</td>
</tr>
<tr>
<td>Oct</td>
<td>PAN</td>
<td>185</td>
<td>0.61 ± 0.48</td>
<td>0.10</td>
<td>0.42</td>
<td>2.99</td>
</tr>
<tr>
<td></td>
<td>PPN</td>
<td></td>
<td>&lt; DL</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>O$_3$</td>
<td>91</td>
<td>16.80 ± 10.0</td>
<td>0.47</td>
<td>18.20</td>
<td>44.80</td>
</tr>
<tr>
<td></td>
<td>CCl$_4$</td>
<td>185</td>
<td>0.073 ± 0.018</td>
<td>0.029</td>
<td>0.066</td>
<td>0.18</td>
</tr>
<tr>
<td>Nov</td>
<td>PAN</td>
<td>195</td>
<td>0.73 ± 0.64</td>
<td>0.14</td>
<td>0.48</td>
<td>3.80</td>
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<tr>
<td></td>
<td>PPN</td>
<td>65</td>
<td>0.18 ± 0.19</td>
<td>DL</td>
<td>0.099</td>
<td>0.89</td>
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<tr>
<td></td>
<td>O$_3$</td>
<td>130</td>
<td>14.10 ± 9.00</td>
<td>2.33</td>
<td>11.43</td>
<td>33.10</td>
</tr>
<tr>
<td></td>
<td>CCl$_4$</td>
<td>195</td>
<td>0.070 ± 0.023</td>
<td>0.038</td>
<td>0.070</td>
<td>0.20</td>
</tr>
<tr>
<td>Dec</td>
<td>PAN</td>
<td>25</td>
<td>0.27 ± 0.16</td>
<td>0.08</td>
<td>0.23</td>
<td>0.86</td>
</tr>
<tr>
<td></td>
<td>PPN</td>
<td></td>
<td>&lt; DL</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>O$_3$</td>
<td>106</td>
<td>18.70 ± 11.80</td>
<td>1.80</td>
<td>22.10</td>
<td>39.70</td>
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<tr>
<td></td>
<td>CCl$_4$</td>
<td>125</td>
<td>0.070 ± 0.012</td>
<td>0.047</td>
<td>0.065</td>
<td>0.11</td>
</tr>
<tr>
<td>Jan</td>
<td>PAN</td>
<td>95</td>
<td>0.29 ± 0.16</td>
<td>0.10</td>
<td>0.25</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>PPN</td>
<td></td>
<td>&lt; DL</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>O$_3$</td>
<td>117</td>
<td>17.40 ± 14.50</td>
<td>1.30</td>
<td>11.60</td>
<td>43.00</td>
</tr>
<tr>
<td></td>
<td>CCl$_4$</td>
<td>95</td>
<td>0.069 ± 0.016</td>
<td>0.054</td>
<td>0.066</td>
<td>0.196</td>
</tr>
<tr>
<td>Feb</td>
<td>PAN</td>
<td>117</td>
<td>1.89 ± 2.08</td>
<td>0.33</td>
<td>1.02</td>
<td>6.76</td>
</tr>
<tr>
<td></td>
<td>PPN</td>
<td>25</td>
<td>0.66 ± 0.32</td>
<td>0.22</td>
<td>0.58</td>
<td>1.45</td>
</tr>
<tr>
<td></td>
<td>O$_3$</td>
<td>117</td>
<td>17.40 ± 14.50</td>
<td>1.30</td>
<td>11.60</td>
<td>43.00</td>
</tr>
<tr>
<td></td>
<td>CCl$_4$</td>
<td>117</td>
<td>0.116 ± 0.049</td>
<td>0.078</td>
<td>0.094</td>
<td>0.30</td>
</tr>
<tr>
<td>Mar</td>
<td>PAN</td>
<td>124</td>
<td>0.69 ± 0.55</td>
<td>0.20</td>
<td>0.41</td>
<td>2.26</td>
</tr>
<tr>
<td></td>
<td>PPN</td>
<td>22</td>
<td>0.10 ± 0.07</td>
<td>0.03</td>
<td>0.09</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td>O$_3$</td>
<td>124</td>
<td>29.90 ± 12.8</td>
<td>1.30</td>
<td>34.30</td>
<td>44.90</td>
</tr>
<tr>
<td></td>
<td>CCl$_4$</td>
<td>124</td>
<td>0.105 ± 0.023</td>
<td>0.083</td>
<td>0.096</td>
<td>0.22</td>
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<tr>
<td>Apr</td>
<td>PAN</td>
<td>183</td>
<td>1.36 ± 0.97</td>
<td>0.20</td>
<td>1.08</td>
<td>4.83</td>
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<tr>
<td></td>
<td>PPN</td>
<td>3</td>
<td>0.11 ± 0.03</td>
<td>0.08</td>
<td>0.13</td>
<td>0.14</td>
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<tr>
<td></td>
<td>O$_3$</td>
<td>185</td>
<td>34.00 ± 13.40</td>
<td>0.90</td>
<td>35.20</td>
<td>75.40</td>
</tr>
<tr>
<td></td>
<td>CCl$_4$</td>
<td>183</td>
<td>0.113 ± 0.038</td>
<td>0.077</td>
<td>0.10</td>
<td>0.28</td>
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<tr>
<td>May</td>
<td>PAN</td>
<td>244</td>
<td>2.29 ± 2.26</td>
<td>0.34</td>
<td>1.35</td>
<td>11.50</td>
</tr>
<tr>
<td></td>
<td>PPN</td>
<td>112</td>
<td>0.77 ± 0.56</td>
<td>0.09</td>
<td>0.56</td>
<td>2.50</td>
</tr>
<tr>
<td></td>
<td>O$_3$</td>
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<td>51.70 ± 17.90</td>
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<td>111.90</td>
</tr>
<tr>
<td></td>
<td>CCl$_4$</td>
<td>244</td>
<td>0.12 ± 0.11</td>
<td>0.059</td>
<td>0.1</td>
<td>1.087</td>
</tr>
<tr>
<td>Jun</td>
<td>PAN</td>
<td>146</td>
<td>3.77 ± 2.82</td>
<td>0.37</td>
<td>2.70</td>
<td>12.10</td>
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<tr>
<td></td>
<td>PPN</td>
<td>78</td>
<td>0.54 ± 0.52</td>
<td>0.08</td>
<td>0.37</td>
<td>2.30</td>
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<tr>
<td></td>
<td>O$_3$</td>
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<td>146.20</td>
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<tr>
<td></td>
<td>CCl$_4$</td>
<td>146</td>
<td>0.152 ± 0.113</td>
<td>0.08</td>
<td>0.116</td>
<td>0.746</td>
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<tr>
<td>Jul</td>
<td>PAN</td>
<td>156</td>
<td>1.86 ± 1.64</td>
<td>0.18</td>
<td>1.28</td>
<td>8.90</td>
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<tr>
<td></td>
<td>PPN</td>
<td>73</td>
<td>0.54 ± 0.33</td>
<td>0.07</td>
<td>0.47</td>
<td>1.83</td>
</tr>
<tr>
<td></td>
<td>O$_3$</td>
<td>150</td>
<td>61.90 ± 28.80</td>
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<td>142.90</td>
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<tr>
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<td>CCl$_4$</td>
<td>156</td>
<td>0.127 ± 0.038</td>
<td>0.091</td>
<td>0.115</td>
<td>0.276</td>
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<tr>
<td>Aug</td>
<td>PAN</td>
<td>219</td>
<td>2.32 ± 1.28</td>
<td>0.26</td>
<td>2.02</td>
<td>6.17</td>
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<td>1.14</td>
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<tr>
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<td>0.181 ± 0.110</td>
<td>0.086</td>
<td>0.153</td>
<td>1.417</td>
</tr>
</tbody>
</table>

DL: Detection limit of PPN (36 pptV).

Fusion condition dominate the atmospheric concentrations of primary pollutants, if the sources’ strength was constant for a pollutant during a day, the diurnal variation of the pollutant would exhibit minimum in noontime or afternoon when fast gas diffusion usually occurs because of elevation of atmospheric boundary layer. The relative stable values of atmospheric CCl$_4$ during the days indicated its fast diffusion in noontime or afternoon was greatly counteracted by its increasing evaporation rates from solvents under elevation of air temperature.
2.3 Correlation between PAN and PPN

Atmospheric PPN and PAN have very similar formation mechanisms through the photochemical reactions of VOCs with NO\textsubscript{x} and would be expected to be strongly correlated. As shown in Fig. 3, significant positive correlations between PAN and PPN in each season were indeed found in this study. The overall correlation between PAN and concurrent PPN during the whole measurement period was quantified by the linear regression as $\text{PPN} = (0.152 \pm 0.005) \text{PAN} - (0.025 \pm 0.022)$ ($N = 440$, $R = 0.84$, $P < 0.0001$). The slope (or the ratio of PPN/PAN) of 0.152 was well within the range (0.135–0.172) reported in polluted areas (Grosjean et al., 1993; Kourtidis et al., 1993; Ridley et al., 1990). The VOCs precursors for PAN have been recognized to be emitted from both anthropogenic and biogenic sources whereas the precursors for PPN (propanal and 1-butene) are predominantly from anthropogenic sources (Grosjean et al., 2001; Roberts et al., 2004). Therefore, the ratio of PPN/PAN has been widely used as an indicator for distinguishing the contribution of anthropogenic hydrocarbons from biogenic hydrocarbons to atmospheric PANs. Through the regression of a linear multivariate correlation involving PAN and PPN, Roberts et al. (2002, 2004) concluded that when the ratio of PPN/PAN is between 13.5% and 17.2%, PANs formation was dominated by anthropogenic hydrocarbons, while dominated by biogenic hydrocarbons when the ratio is lower than 10%. The average ratio of PPN/PAN (15.2%) obtained by this study implied that the PANs formation in Beijing was dominated by anthropogenic hydrocarbons emission.

2.4 Correlation between PAN and \(O_3\)

The net production of \(O_3\) in the troposphere is derived from the photochemical conversion of NO to NO\textsubscript{2} through the organic peroxy radical oxidation. Peroxyacetyl radical, as an important component of peroxy radicals, also participates in \(O_3\) production, and generates PAN via its reaction with NO\textsubscript{2} in the atmosphere. Therefore, a positive correlation between PAN and \(O_3\) is expected and has been reported in the summer and autumn daytime in Beijing (Liu et al., 2010; Wang and Zhang, 2007; Yang et al.,
and in other urban areas, i.e., Porto Alegre, Brazil (Grosjean et al., 2002) and Munich (Rappenglück et al., 1993).

In this study, only the data between 11:00–16:00 local time when photochemical reactions are most intensive were analyzed for demonstrating the correlation between PAN and O3. The linear correlation coefficients (R) and the slopes (ΔO3/ΔPAN) of the correlations in each month are illustrated in Fig. 4. The fairly positive correlations between PAN and O3 were found from May to September with R ranging from 0.56 to 0.92, indicating that both atmospheric PAN and O3 in Beijing during these photochemical reactive months were dominated by local formation. No significant correlations were found in March, April, October and November with R ranging from −0.2 to 0.2, indicating that atmospheric PAN and O3 might be governed by complex sources, including local photochemical formation, long range transportation, diffusion from the upper atmosphere. Significant negative correlations were found in the three winter months (December, January, and February) with R ranging from −0.69 to −0.75. During winter season in Beijing, photochemical reactivity becomes extremely low as shown the extremely low concentrations of O3 and PAN. In addition, the atmospheric boundary in winter becomes low, which favors for pollutants accumulation, for example, the most frequent haze days have been found during winter in Beijing (Sun et al., 2006; Wang et al., 2006). The accumulation of NO emitted from vehicle exhaust could consume large quantity of O3 through titration reaction, whereas PAN consumption through thermal decomposition coupling with NO reaction became extremely low as the low temperature in winter. Both the accumulation of PAN formed through weak photochemical reactions (mainly initiated by OH from HONO photolysis) and consumption of O3 by NO were responsible for the significant negative correlations during winter seasons. A similar yearly trend of ΔO3/ΔPAN was also observed in 2-years data recorded at the upper Midwest site (Pippin et al., 2001) and in 5-years data obtained at a rural site in eastern Canada (Bottenheim et al., 1994).

The ΔO3/ΔPAN values obtained by this study in the summer months were 9.92–18.0, which were close to the value of 18.87 reported by Zhang et al. (2011) in August 2006 in Beijing, but were generally lower than the values reported in other cities (e.g. 24.3 reported at an urban site of Ontario by Shepson et al., 1992), in forest regions (e.g., 38.2–81.9 reported by Pippin et al., 2001), and at rural sites (e.g. 39.01 reported by Hartsell et al., 1994). Shepson et al. (1992) found ΔO3/ΔPAN increased substantially from urban (24.3) to rural (70.6) air masses, Pippin et al. (2001) also found that the extremely greater values (ΔO3/ΔPAN: 76.6–81.9) observed in summer of 1998 than those (ΔO3/ΔPAN: 38.2–45.1) observed in summer of 1997 was consistent with regions impacted by less polluted air masses. Therefore, the ΔO3/ΔPAN can be used as an indicator for air pollution status, that is, the less values of ΔO3/ΔPAN mean serious pollution. As compared above, the relatively low values of ΔO3/ΔPAN in summers of Beijing implied that Beijing is suffering serious air pollution.

### 3 Conclusions

Atmospheric PAN, PPN, O3, and CCl4 were simultaneously measured from September 2010 to August 2011 in Beijing. The common seasonal variations of the pollutants revealed that high values usually occurred from late spring to early autumn and minimal values in winter. The seasonal variations of PAN, PPN and O3, typical secondary pollutants, well reflected the seasonal variation trend of photochemical reactivity in Beijing, and that of CCl4,
typical primary pollutant, revealed that air temperature is the dominant factor affecting CCl₄ evaporation from solvents. The abnormal high values of PAN, PPN and CCl₄ observed in February were ascribed to the accumulation of the pollutants formed from weak photochemical reactions for PAN and PPN or primary emission for CCl₄ under the frequent haze days occurred in the month.

The significant positive correlation between PAN and PPN during the whole investigating period further confirmed that they are from similar formation mechanisms, and the ratio of ΔO₃/ΔPAN indicated anthropogenic VOCs were their dominant precursors in the megacity.

PAN and O₃ exhibited a strong positive correlation in the summer with ΔO₃/ΔPAN ranging from 9.92 to 18.0. In comparison with other measurements in different areas, the relatively low values of ΔO₃/ΔPAN in Beijing indicated serious air pollution in the megacity. The strong negative correlation between PAN and O₃ in the months of winter reflected strong O₃ consumption by NO titration and less thermal decomposition of PAN.

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