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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 (CCl_4) 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 CCl_4 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 O_3 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 ($R = 0.91$), spring ($R = 0.94$), and summer ($R = 0.81$), 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 O_3 in summer with the low slopes ($\Delta\text{O}_3/\Delta\text{PAN}$) ranging from 9.92 to 18.0 indicated serious air pollution in Beijing, and strong negative correlation in winter reflected strong O_3 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)OONO_2) are crucial components of the odd-nitrogen compounds (NO_y) in the atmosphere and particularly important secondary pollutants formed via photochemical reactions of volatile organic compounds (VOCs) in the presence of NO_x (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 to the plant than that of O_3 (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 O_3 (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

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transported over long distances from polluted continental regions into the remote areas where they release NO_x under high temperature (Honrath et al., 1996; Kondo et al., 1997; Singh et al., 1996), and hence PANs act as important temporary NO_x 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 chlorofluorocarbons 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). The information about operation condition and calibration of the instrument was essentially identical to our previous study (Zhang et al., 2012). Briefly, the GC oven and detector temperatures were maintained at 20°C and 38°C respectively. The carrier gas helium (99.999%) and make-up gas N₂ (99.999%) flow rates were adjusted to be 8 and 54 mL/min, respectively. Air sample was drawn into the GC loop (0.5 mL) by a minipump (NMP830KNDC, KNF Inc.) via 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 NO_x

The measurements of ambient ozone and NO_x were simultaneously conducted from September 2010 to August 2011 using Model 49i ozone analyzer and Model 42i NO_x 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 NO_x analyzer, it was achieved by Thermo Scientific Model 146i with NO standard gas. The detection limit (3S/N) for NO_x measurement was 0.4 ppbV, and the total measurement uncertainty was estimated to be 5%.

Fig. 1 Monthly variations of PAN, PPN, O₃, CCl₄ and Temperature. Monthly averages (with error bar ($\pm 1 \sigma$) for temperature), medians (dashes in the rectangles), 25th percent (bottom of rectangles), and 75th (top of rectangles).

2 Results and discussion

2.1 Monthly variations

The monthly variations of PAN, PPN, O₃, and CCl₄ 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 NO_x, 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)).

The abnormal high concentrations of PAN and PPN in February, especially on the haze days (e.g., on 23 February their daily mean concentrations were as high as 5.71 ppbV and 0.68 ppbV, respectively), also indicated that high OH radicals existed in the atmosphere because of PAN and PPN exclusively from secondary formation. Due to the weak sunlight and low concentration of O_3 on haze days, the sources of OH from photolysis of O_3 and HCHO as well as the reactions of O_3 with unsaturated alkenes should be negligible. Because photolysis of HONO can easily form OH radical under weak sunlight irradiation, HONO formed from the heterogeneous reaction of NO_2 on air particle surface was suspected to be responsible for the high OH concentration in haze days. The maximal monthly average concentrations of PAN and PPN were observed in September, while O_3 occurred in August. Although formation potentials for PAN and PPN in August should be greater than in September due to stronger sunlight irradiation, the thermal decomposition of them under higher temperature in August would greatly counteract their formation potentials. In contrast, O_3 is a thermal stable compound, and the atmospheric concentrations of O_3 mainly depend upon photochemical reactivity which has been found to be greatest in August in Beijing (Gao and Zhang, 2012). Although PAN and PPN have very similar formation mechanisms, the monthly variations of them were not identical due to their different VOCs precursors, e.g., the second maximal average values for PAN and PPN appeared in July and in May, respectively. As for CCl_4 , the monthly variation was similar to air temperature, indicating atmospheric CCl_4 in Beijing was mainly from evaporation of solvents. Because air temperature reflects both sunlight intensity and evaporation rates for solvents, the monthly variation of CCl_4 , only with the exception in February, was almost concurrent with that of O_3 . As mentioned above, frequent haze days occurred in the February, which favored for pollutants accumulation, e.g., the daily mean concentration of CCl_4 achieved to extremely high value of 190.4 pptV on 23 February.

To compare with previous studies in Beijing, more detail information about the sample number, the mean, median and maximal values in each month are summarized in **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, O₃ and CCl₄ in each month (unit: ppbV)

Month	Species	N	Mean ± SD	Min	Median	Max
Sep	PAN	228	3.98 ± 2.93	0.20	3.49	12.52
	PPN	16	1.14 ± 0.39	0.75	0.96	2.16
	O ₃	88	45.0 ± 25.9	5.13	42.47	98.00
	CCl ₄	228	0.078 ± 0.055	0.021	0.057	0.47
Oct	PAN	185	0.61 ± 0.48	0.10	0.42	2.99
	PPN	–	< DL	< DL	< DL	< DL
	O ₃	91	16.80 ± 10.0	0.47	18.20	44.80
	CCl ₄	185	0.073 ± 0.018	0.029	0.066	0.18
Nov	PAN	195	0.73 ± 0.64	0.14	0.48	3.80
	PPN	65	0.18 ± 0.19	DL	0.099	0.89
	O ₃	130	14.10 ± 9.00	2.33	11.43	33.10
	CCl ₄	195	0.078 ± 0.023	0.038	0.070	0.20
Dec	PAN	25	0.27 ± 0.16	0.08	0.23	0.86
	PPN	–	< DL	< DL	< DL	–
	O ₃	106	18.70 ± 11.80	1.80	22.10	39.70
	CCl ₄	125	0.070 ± 0.012	0.047	0.065	0.11
Jan	PAN	95	0.29 ± 0.16	0.10	0.25	0.72
	PPN	–	< DL	< DL	< DL	< DL
	O ₃	95	18.60 ± 13.10	2.20	16.60	40.70
	CCl ₄	95	0.069 ± 0.016	0.054	0.066	0.196
Feb	PAN	117	1.89 ± 2.08	0.33	1.02	6.76
	PPN	25	0.66 ± 0.32	0.22	0.58	1.45
	O ₃	117	17.40 ± 14.50	1.30	11.60	43.00
	CCl ₄	117	0.116 ± 0.049	0.078	0.094	0.30
Mar	PAN	124	0.69 ± 0.55	0.20	0.41	2.26
	PPN	22	0.10 ± 0.07	0.03	0.09	0.34
	O ₃	124	29.9 ± 12.8	1.30	34.30	44.90
	CCl ₄	124	0.105 ± 0.023	0.083	0.096	0.22
Apr	PAN	183	1.36 ± 0.97	0.20	1.08	4.83
	PPN	3	0.11 ± 0.03	0.08	0.13	0.14
	O ₃	185	34.00 ± 13.40	0.90	35.20	75.40
	CCl ₄	183	0.113 ± 0.038	0.077	0.10	0.28
May	PAN	244	2.29 ± 2.26	0.34	1.35	11.50
	PPN	112	0.77 ± 0.56	0.09	0.56	2.50
	O ₃	243	51.70 ± 17.90	7.10	51.60	111.90
	CCl ₄	244	0.12 ± 0.1	0.059	0.1	1.087
Jun	PAN	146	3.77 ± 2.82	0.37	2.70	12.10
	PPN	78	0.56 ± 0.52	0.08	0.37	2.30
	O ₃	146	72.10 ± 38.4	10.5	65.4	146.20
	CCl ₄	146	0.152 ± 0.113	0.08	0.116	0.746
Jul	PAN	156	1.86 ± 1.64	0.18	1.28	8.90
	PPN	73	0.54 ± 0.33	0.07	0.47	1.83
	O ₃	150	61.90 ± 28.80	10.90	51.90	142.90
	CCl ₄	156	0.127 ± 0.038	0.091	0.115	0.276
Aug	PAN	219	2.32 ± 1.28	0.26	2.02	6.17
	PPN	46	0.38 ± 0.23	0.09	0.34	1.14
	O ₃	217	84.10 ± 35.40	6.90	84.40	173
	CCl ₄	219	0.181 ± 0.110	0.086	0.153	1.417

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 CCl₄ 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.

Fig. 2 Diurnal patterns of PAN, O₃, and CCl₄ during the autumn of 2010 to the summer of 2011. Error bars represent standard deviations.

2.3 Correlation between PAN and PPN

Atmospheric PPN and PAN have very similar formation mechanisms through the photochemical reactions of VOCs with NO_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 $PPN = (0.152 \pm 0.005) PAN - (-0.025 \pm 0.022)$ ($N = 440$, $R = 0.84$, $P < 0.0001$). 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 O₃

The net production of O₃ in the troposphere is derived from the photochemical conversion of NO to NO₂ through the organic peroxy radical oxidation. Peroxyacetyl radical, as an important component of peroxy radicals, also participates in O₃ production, and generates PAN via its reaction with NO₂ in the atmosphere. Therefore, a positive correlation between PAN and O₃ 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.,

Fig. 3 Linear regressions between PAN and concurrent PPN as a function of season.

2009) and in other urban areas, i.e., Porto Alegre, Brazil (Grosjean et al., 2002) and Munich (Rappengluck 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 O_3 . The linear correlation coefficients (R) and the slopes ($\Delta O_3/\Delta PAN$) of the correlations in each month are illustrated in **Fig. 4**. The fairly positive correlations between PAN and O_3 were found from May to September with R ranging from 0.56 to 0.92, indicating that both atmospheric PAN and O_3 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 O_3 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 O_3 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 O_3 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 O_3 by NO were responsible for the significant negative correlations during

Fig. 4 PAN/ O_3 slope plotted as a function of month. The error bars represented the 1σ deviation for the slopes. The determined coefficient R was shown for the monthly linear regression.

winter seasons. A similar yearly trend of $\Delta O_3/\Delta PAN$ 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 $\Delta O_3/\Delta PAN$ 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 $\Delta O_3/\Delta PAN$ increased substantially from urban (24.3) to rural (70.6) air masses, Pippin et al. (2001) also found that the extremely greater values ($\Delta O_3/\Delta PAN$: 76.6–81.9) observed in summer of 1998 than those ($\Delta O_3/\Delta PAN$: 38.2–45.1) observed in summer of 1997 was consistent with regions impacted by less polluted air masses. Therefore, the $\Delta O_3/\Delta PAN$ can be used as an indicator for air pollution status, that is, the less values of $\Delta O_3/\Delta PAN$ mean serious pollution. As compared above, the relatively low values of $\Delta O_3/\Delta PAN$ in summers of Beijing implied that Beijing is suffering serious air pollution.

3 Conclusions

Atmospheric PAN, PPN, O_3 , and CCl_4 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 O_3 , typical secondary pollutants, well reflected the seasonal variation trend of photochemical reactivity in Beijing, and that of CCl_4 ,

typical primary pollutant, revealed that air temperature is the dominant factor affecting CCl_4 evaporation from solvents. The abnormal high values of PAN, PPN and CCl_4 observed in February were ascribed to the accumulation of the pollutants formed from weak photochemical reactions for PAN and PPN or primary emission for CCl_4 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 $\Delta\text{O}_3/\Delta\text{PAN}$ indicated anthropogenic VOCs were their dominant precursors in the megacity.

PAN and O_3 exhibited a strong positive correlation in the summer with $\Delta\text{O}_3/\Delta\text{PAN}$ ranging from 9.92 to 18.0. In comparison with other measurements in different areas, the relatively low values of $\Delta\text{O}_3/\Delta\text{PAN}$ in Beijing indicated serious air pollution in the megacity. The strong negative correlation between PAN and O_3 in the months of winter reflected strong O_3 consumption by NO titration and less thermal decomposition of PAN.

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REFERENCES

- Aikin A C, Herman J R, Maier E J, Mcquillan C J, 1982. Atmospheric chemistry of ethane and ethylene. *Journal of Geophysical Research-Oceans and Atmospheres*, 87(C4): 3105–3118.
- Altshuller A P, 1976. Average tropospheric concentration of carbon tetrachloride based on industrial production, usage, and emissions. *Environmental Science and Technology*, 10(6): 596–598.
- Altshuller A P, 1978. Assessment of the contribution of chemical species to the eye irritation potential of photochemical smog. *Journal of the Air Pollution Control Association*, 28(6): 594–598.
- Barletta B, Meinardi S, Simpson I J, Sherwood R F, Chan C Y, Wang X et al., 2006. Ambient halocarbon mixing ratios in 45 Chinese cities. *Atmospheric Environment*, 40(40): 7706–7719.
- Bottenheim J W, Sirois A, Brice K A, Gallant A J, 1994. Five years of continuous observations of PAN and ozone at a rural location in eastern Canada. *Journal of Geophysical Research-Atmospheres*, 99(D3): 5333–5352.
- Cox R A, Derwent R G, Eggleton A E J, Lovelock J E, 1976. Photochemical oxidation of halocarbons in the troposphere. *Atmospheric Environment*, 10(4): 305–308.
- Derwent R, Simmonds P, O'doherty S, Ryall D, 1998. The impact of the Montreal protocol on halocarbon concentrations in northern hemisphere baseline and European air masses at Mace Head, Ireland over a ten year period from 1987–1996. *Atmospheric Environment*, 32(21): 3689–3702.
- Gaffney J S, Marley N A, 2001a. Comment on “Environmental implications on the oxygenation of gasoline with ethanol in the metropolitan area of Mexico City”. *Environmental Science and Technology*, 35(24): 4957–4958.
- Gaffney J S, Marley N A, 2001b. Peroxyacetyl nitrate (PAN): historical perspective. In: Proceedings of the 81stAMS Annual Meeting. A Millennium Symposium on Atmospheric Chemistry. Albuquerque, NM. 14–19 January.
- Gao Y, Zhang M G, 2012. Sensitivity analysis of surface ozone to emission controls in Beijing and its neighboring area during the 2008 Olympic Games. *Journal of Environmental Sciences*, 24(1): 50–61.
- Grosjean D, Williams E L, Grosjean E, 1993. Peroxyacetyl nitrates at southern California mountain forest locations. *Environmental Science and Technology*, 27(1): 110–121.
- Grosjean E, Grosjean D, Woodhouse L F, 2001. Peroxyacetyl nitrate and peroxypropionyl nitrate during SCOS97-NARSTO. *Environmental Science and Technology*, 35(20): 4007–4014.
- Grosjean E, Grosjean D, Woodhouse L F, Yang Y J, 2002. Peroxyacetyl nitrate and peroxypropionyl nitrate in Porto Alegre, Brazil. *Atmospheric Environment*, 36(14): 2405–2419.
- Hansel A, Wisthaler A, 2000. A method for real-time detection of PAN, PPN and MPAN in ambient air. *Geophysical Research Letters*, 27(6): 895–898.
- Happell J D, Roche M P, 2003. Soils: A global sink of atmospheric carbon tetrachloride. *Geophysical Research Letters*, 30(2): 1088.
- Hartsell B E, Aneja V P, Lonneman W A, 1994. Relationships between peroxyacetyl nitrate, O_3 , and NO_y at the rural southern oxidants study site in central piedmont, North-Carolina, Site Sonia. *Journal of Geophysical Research-Atmospheres*, 99(D10): 21033–21041.
- Honrath R E, Hamlin A J, Merrill J T, 1996. Transport of ozone precursors from the Arctic troposphere to the North Atlantic region. *Journal of Geophysical Research-Atmospheres*, 101(D22): 29335–29351.
- Kleindienst T E, Shepson P B, Smith D F, Hudgens E E, Nero C M, Cupitt L T et al., 1990. Comparison of mutagenic activities of several peroxyacetyl nitrates. *Environmental and Molecular Mutagenesis*, 16(2): 70–80.
- Kondo Y, Koike M, Kawakami S, Singh H B, Nakajima H, Gregory G L et al., 1997. Profiles and partitioning of reactive nitrogen over the Pacific Ocean in winter and early spring. *Journal of Geophysical Research*, 102(D23): 28405–28424.
- Kourtidis K A, Fabian P, Zerefos C, Rappengluck B, 1993. Peroxyacetyl nitrate (PAN), peroxypropionyl nitrate (PPN) and PAN/ozone ratio measurements at 3 sites in Germany. *Tellus Series B-Chemical and Physical Meteorology*, 45(5): 442–457.
- Lee G, Jang Y, Lee H, Han J S, Kim K R, Lee M, 2008. Characteristic behavior of peroxyacetyl nitrate (PAN) in Seoul megacity, Korea. *Chemosphere*, 73(4): 619–628.
- Liu Z, Wang Y H, Gu D S, Zhao C, Huey L G, Stickel R et al., 2010. Evidence of reactive aromatics as a major source of peroxy acetyl nitrate over China. *Environmental Science and Technology*, 44(18): 7017–7022.
- Lovelock J E, Maggs R J, Wade R J, 1973. Halogenated hydrocarbons in and over the Atlantic. *Nature*, 241(5386): 194–196.
- Marley N A, Gaffney J S, Ramos-Villegas R, Gonzalez B C, 2007. Comparison of measurements of peroxyacetyl nitrates and primary carbonaceous aerosol concentrations in Mexico City determined in 1997 and 2003. *Atmospheric Chemistry and Physics*, 7(9): 2277–

- 2285.
- McFadyen G G, Cape J N, 2005. Peroxyacetyl nitrate in eastern Scotland. *Science of the Total Environment*, 337(1-3): 213–222.
- Molina M J, Rowland F S, 1974. Stratospheric sink for chlorofluoromethanes: Chlorine atomcatalysed destruction of ozone. *Nature*, 249(5460): 810–812.
- Pang X B, Mu Y J, 2006. Seasonal and diurnal variations of carbonyl compounds in Beijing ambient air. *Atmospheric Environment*, 40(33): 6313–6320.
- Pippin M, Bertman S, Thornberry T, Town M, Carroll M A, Sillman S, 2001. Seasonal variations of PAN, PPN, and O₃ at the upper Midwest PROPHET site. *Journal of Geophysical Research-Atmospheres*, 106(D20): 24451–24463.
- Rappengluck B, Kourtidis K, Fabian P, 1993. Measurements of ozone and peroxyacetyl nitrate (PAN) in Munich. *Atmospheric Environment Part B-Urban Atmosphere*, 27(3): 293–305.
- Ridley B A, Shetter J D, Walega J G, Madronich S, Elsworth C M, Grahek F E et al., 1990. The behavior of some organic nitrates at Boulder and Niwot Ridge, Colorado. *Journal of Geophysical Research-Atmospheres*, 95(D9): 13949–13961.
- Roberts J M, Flocke F, Chen G, de Gouw J, Holloway J S, Hubler G et al., 2004. Measurement of peroxydicarboxylic nitric anhydrides (PANs) during the ITCT 2K2 aircraft intensive experiment. *Journal of Geophysical Research-Atmospheres*, 109(D23). DOI: 10.1029/2004JD004960.
- Roberts J M, Flocke F, Stroud C A, Hereid D, Williams E, Fehsenfeld F et al., 2002. Ground-based measurements of peroxydicarboxylic nitric anhydrides (PANs) during the 1999 southern oxidants study Nashville intensive. *Journal of Geophysical Research-Atmospheres*, 107(D21): 1–10.
- Roberts J M, Tanner R L, Newman L, Bowersox V C, Bottenheim J W, Anlauf K G et al., 1995. Relationships between PAN and ozone at sites in eastern North-America. *Journal of Geophysical Research-Atmospheres*, 100(D11): 22821–22830.
- Shao M, Lu S H, Liu Y, Xie X, Chang C C, Huang S et al., 2009. Volatile organic compounds measured in summer in Beijing and their role in ground-level ozone formation. *Journal of Geophysical Research-Atmospheres*, 114(D2). DOI: 10.1029/2008JD010863.
- Shepson P B, Hastie D R, So K W, Schiff H I, 1992. Relationships between PAN, PPN and O₃ at urban and rural sites in Ontario. *Atmospheric Environment Part A-General Topics*, 26(7): 1259–1270.
- Shepson P B, Kleindienst T E, Edney E O, Nero C M, Cupitt L T, Claxton L D, 1986. Acetaldehyde: the mutagenic activity of its photooxidation products. *Environmental Science and Technology*, 20(10): 1008–1013.
- Simmonds P, Cunnold D, Alyea F, Cardelino C, Crawford A, Prinn R et al., 1988. Carbon tetrachloride lifetimes and emissions determined from daily global measurements during 1978–1985. *Journal of Atmospheric Chemistry*, 7(1): 35–58.
- Singh H B, 1987. Reactive nitrogen in the troposphere. *Environmental Science and Technology*, 21(4): 320–327.
- Singh H B, Hanst P L, 1981. Peroxyacetyl nitrate (PAN) in the unpolluted atmosphere—An important reservoir for nitrogen-oxides. *Geophysical Research Letters*, 8(8): 941–944.
- Singh H B, Herlth D, Kolyer R, Salas L, Bradshaw J D, Sandholm S T et al., 1996. Reactive nitrogen and ozone over the western Pacific: distribution, partitioning, and sources. *Journal of Geophysical Research-Atmospheres*, 101(D1): 1793–1808.
- Singh H B, Herlth D, Ohara D, Salas L, Torres A L, Gregory G L et al., 1990. Atmospheric peroxyacetyl nitrate measurements over the Brazilian Amazon basin during the wet season—relationships with nitrogen-oxides and ozone. *Journal of Geophysical Research-Atmospheres*, 95(D10): 16945–16954.
- Singh H B, Ohara D, Herlth D, Bradshaw J D, Sandholm S T, Gregory G L et al., 1992. Atmospheric measurements of peroxyacetyl nitrate and other organic nitrates at high latitudes: possible sources and sinks. *Journal of Geophysical Research-Atmospheres*, 97(D15): 16511–16522.
- Sun E J, Huang M H, 1995. Detection of peroxyacetyl nitrate at phytotoxic level and its effects on vegetation in Taiwan. *Atmospheric Environment*, 29(21): 2899–2904.
- Sun X Z, Wan D, Shi Y H, Zhang J B, Hu J X, 2010. Concentrations and trends of CFCs and CCl₄ in the atmosphere of Beijing. *Research of Environmental Science*, 23(6): 674–679.
- Sun Y, Zhuang G, Tang A, Wang Y, An Z, 2006. Chemical characteristics of PM_{2.5} and PM₁₀ in haze-fog episodes in Beijing. *Environmental Science and Technology*, 40(10): 3148–3155.
- Tang G, Li X, Wang Y, Xin J, Ren X, 2009. Surface ozone trend details and interpretations in Beijing, 2001–2006. *Atmospheric Chemistry and Physics*, 9(22): 8813–8823.
- Taylor O, 1969. Importance of peroxyacetyl nitrate (PAN) as a phytotoxic air pollutant. *Journal of the Air Pollution Control Association*, 19(5): 347–351.
- Wang B, Shao M, Roberts J M, Yang G, Yang F, Hu M et al., 2010. Ground-based on-line measurements of peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN) in the Pearl River Delta, China. *International Journal of Environmental Analytical Chemistry*, 90(7): 548–559.
- Wang B, Zhang J B, 2007. Monitoring and analysis of PAN and PPN in the air of Beijing during the summer of 2005. *Environmental Science*, 28(7): 1621–1626.
- Wang T, Ding A J, Gao J, Wu W S, 2006. Strong ozone production in urban plumes from Beijing, China. *Geophysical Research Letters*, 33(21). DOI: 10.1029/2006GL027689.
- Wang Y, Zhuang G S, Sun Y L, An Z S, 2006. The variation of characteristics and formation mechanisms of aerosols in dust, haze, and clear days in Beijing. *Atmospheric Environment*, 40(34): 6579–6591.
- Watanabe I, Nakanishi M, Tomita J, Hatakeyama S, Murano K, Mukai H et al., 1998. Atmospheric peroxyacetyl nitrates in urban/remote sites and the lower troposphere around Japan. *Environmental Pollution*, 102(1): 253–261.
- Williams E L, Grosjean D, 1991. Peroxypropionyl nitrate at a southern California mountain forest site. *Environmental Science and Technology*, 25(4): 653–659.
- Xu Z, Zhang J, Yang G, Hu M, 2011. Acyl peroxy nitrate measurements during the photochemical smog season in Beijing, China. *Atmospheric Chemistry and Physics Discussion*, 11(3): 10265–10303.
- Yang G, Zhang J B, Wang B, 2009. Analysis on correlation and concentration variation of atmospheric PAN and PPN in Beijing. *Acta Scientiarum Naturalium Universitatis Pekinensis*, 45(1): 144–150.
- Yao B, Zhou L X, Zhang F, Xu L, Zang K P, Zhang X C et al., 2010. In-situ measurement of atmospheric carbon tetrachloride (CCl₄) at the Shangdianzi global atmosphere watch regional station. *Acta*

- Scientiae Circumstantiae*, 30(12): 2377–2382.
- Zhang G, Mu Y, Liu J, Mellouki A, 2012. Direct and simultaneous determination of trace-level carbon tetrachloride, peroxyacetyl nitrate, and peroxypropionyl nitrate using gas chromatography-electron capture detection. *Journal of Chromatography A*, 1266: 110–115.
- Zhang J, Xu Z, Yang G, Wang B, 2011. Peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN) in urban and suburban atmospheres of Beijing, China. *Atmospheric Chemistry and Physics Discussions*, 11(3): 8173–8026.
- Zhang J B, Tang X Y, 1994. Atmospheric PAN measurements and the formation of PAN in various systems. *Environmental Chemistry*, 13(1): 30–39.
- Zhang J M, Wang T, Ding A J, Zhou X H, Xue L K, Poon C N et al., 2009. Continuous measurement of peroxyacetyl nitrate (PAN) in suburban and remote areas of western China. *Atmospheric Environment*, 43(2): 228–237.
- Zhang Y C, Hu H L, Tan K, Liu X Q, Shao S S, Yang G C et al., 2004. Dial measurements of SO₂, NO₂, and O₃ in Beijing. In: Proceedings of the 22nd International Laser Radar Conference (Ilrc 2004). Matera, Italy. 12–16 July. Vols 1 and 2, 561: 721–724.
- Zurer P S, 1995. Delayed CFC phase out in developing-countries raises growing concern. *Chemical and Engineering News*, 73(19): 25–26.