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Source analysis of peroxyacetyl nitrate (PAN) in Guangzhou, China: a yearlong observation study

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Abstract

In recent years, photochemical smog has been a major cause of air pollution in the metropolitan area of Guangzhou, China, with a continuing increase in the concentrations of photochemical pollutants. The concentration of peroxyacetyl nitrate (PAN) has

- ⁵ often been found to reach very high levels, posing a potential threat to the public health. To better understand the changes in PAN concentration and its sources, a study was carried from January to December of 2012 at the Guangzhou Panyu Atmospheric Composition Station (GPACS) to measure the atmospheric concentrations of PAN as well as those of ozone (O_3), nitrogen oxides (NO_x), and non-methane hydrocarbon (NMHC).
- These data were analyzed to investigate the quantitative relationships between PAN and its precursors. In the study period, the hourly concentrations of PAN varied from below instrument detection limit to 12.0 ppbv. The yearly mean concentration of PAN was 0.84 ppbv, with the daily mean concentration exceeding 5 ppbv in 32 of the total observation days. Calculations indicate that among the measured NMHC species,
- ¹⁵ alkenes accounted for 53 % of the total NMHC contribution to the PAN production, with aromatics and alkanes accounting for about 11 and 7 % of the total, respectively. During the period of our observation only a modest correlation was found between the concentrations of PAN and O₃ for daytime hours, and observed PAN concentrations were relatively high even though the observed NMHCs / NO_x ratio was low. This suggests
- regional air mass transport of pollutants had a major impact on the PAN concentrations in Guangzhou area.

1 Introduction

Peroxyacetyl nitrate ($CH_3C(O)O_2NO_2$, PAN) is one of the products of photochemical reactions in the troposphere (Roberts, 2007). It plays an important role in many atmospheric processes and has a major impact on urban and regional air quality (Nielsen

spheric processes and has a major impact on urban and regional air quality (Nielsen et al., 1981; Kourtidis et al., 1993; Williams II et al., 1990). PAN is highly toxic and is

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harmful to human health at a concentration as low as 5 ppbv (Taylor et al., 1969; WHO, 1987; Sun and Huang, 1995).

The formation of PAN in the atmosphere begins with reactions of volatile organic compounds (VOCs) with hydroxyl (OH) radical (Reaction R1a) or photolysis of VOCs

to produce peroxyacetyl (PA) radicals (Reactions R1b, R1c), which then react with nitrogen dioxide (NO₂) to form PAN (R2).

 $CH_3CHO + OH \xrightarrow{O_2} CH_3C(O)OO + H_2O$ (R1a)

 $CH_{3}(O)CH_{3} + h\nu \xrightarrow{O_{2}} CH_{3}C(O)OO + CH_{3}$ (R1b)

¹⁰
$$CH_3COCHO + hv \xrightarrow{O_2} CH_3C(O)OO + HCO$$
 (R1c)

 $CH_3C(O)OO + NO_2 + M \rightarrow CH_3C(O)O_2NO_2 + M$

Other acyl peroxy nitrates (RC(O)OONO₂) are also formed from the oxidation of VOCs, but with a much lower yields. In the atmosphere, PAN accounts for 75–90% of the total acyl peroxy nitrates (Roberts et al., 2002, 2007; Wolfe et al., 2007) and is a dominant organic nitrate reservoir (Roberts et al., 1995; Bertram et al., 2013).

Different VOC precursors affect the PAN formation differently (Derwent and Jenkin, 1991). For example, isoprene, which has a high chemical reactivity and can strongly

- ²⁰ impact the PA radical production (Altshuller, 1993; Roberts et al., 2001, 2002, 2006; Cleary et al., 2007), is a major precursor of PAN (Folberth et al., 2006; Fischer et al., 2014; Horowitz et al., 1998); on the other hand, recent research has shown that aromatic compounds of relatively low reactivity are also important to the production of PAN (Grosjean et al., 2002; Liu et al., 2010).
- PAN is removed from the atmosphere through a number of processes. Removal of PAN from the atmosphere through atmospheric deposition potentially is an important source of nitrogen for plants (Schrimpf et al., 1996; Sparks et al., 2003; Wolfe et al., 2009) and can have a significant impact on ecosystem productivity and soil acidification 17095

(Goulding et al., 1998; Magnani et al., 2007). The main mechanisms for PAN removal from the atmosphere are thermal decomposition and UV photolysis (Singh et al., 1987; Tuazon et al., 1991; Talukdar et al., 1995). At low latitudes, where temperature is high

- and UV radiation is relatively low, thermal decomposition dominates the PAN consumption. At night or in the winter, because of its stability at low temperature, PAN can be transported for long distances and, when temperature rises, decompose to release NO_x , thus becoming a source of radicals (Singh and Salas, 1989; Beine et al., 2000) and affecting regional O_3 formation (Crutzen, 1979; Ridley et al., 1990; Hudman et al., 2004).
- ¹⁰ In the troposphere, nearly all of the PAN is produced by photochemical reactions. Therefore, PAN is often considered a better indicator of photochemical processes compared to O_3 , which can come from a number of sources and processes (Bottenheim et al., 1994; McFadyen and Cape, 2005; Nieboer et al., 1976). In smog chamber experiments, both PAN and O_3 are formed from reactions of NO_x and VOCs following
- ¹⁵ similar photochemical mechanisms (Pitts et al., 1975; Spicer, 1982). This suggests that there should exist a correlation between the concentrations of these two pollutants in polluted urban airs. Although studies have found that the PAN concentration in many environments closely follows the O_3 concentration (e.g., Tsani-Bazaca et al., 1988; Glavas et al., 2001; Zhang et al., 2009), other studies have failed to show a correlation
- ²⁰ between the concentrations of these two characteristic photochemical products (e.g., Kourtidis et al.,1993; Rappengluck et al.,1993; McFadyen and Cape, 2005; Liu et al., 2010; Wang et al., 2010), suggesting the possible presence of other sources of PAN and/or O₃ in addition to local photochemical reactions.

Over the last three decades, the air quality of the metropolitan area of Guangzhou in south China has been deteriorating as the result of high emissions of air pollutants, higher temperatures, high relative humidity, and strong solar radiation (Wu et al., 2009). In recent years, severe photochemical pollution episodes occur frequently and now is a major focus of the city's air pollution control effort. Among the important photochemical pollutants monitored in Guangzhou, PAN has often been found to reach high con-

(R2)

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centrations in the air, posing potential harm to public health. Although recently there have been a number of studies of PAN in China and its surrounding areas, they were largely limited to the severe smog episodes (Watanabe et al., 2000; Lee et al., 2008; Wang et al., 2010; Zhang et al., 2009; J. B. Zhang et al., 2011). Little effort has been doubted to approximate a particular of PAN and related plateate and related plateate in the

devoted to continuous observations of PAN and related photochemical pollutants in the area's atmosphere.

We have carried out a year-long observation study in Guangzhou to collect time series concentration data of PAN, O_3 , NO_x and non-methane hydrocarbons (NMHCs) as well as meteorological data. Using these data, we examined the variation of PAN con-

centration over an entire year and the relationship between PAN and other photochemical pollutants (O_3 , NO_x , and NMHCs). Based on the observed NMHC concentrations, we also evaluated the contributions of different NMHC species to the production of PAN. Results of this study will provide useful information for more effectively managing the air quality of Guangzhou and the surrounding areas.

15 2 Experimental

2.1 Experiment site

This study was conducted at Guangzhou Panyu Atmospheric Composition Station (GPACS) from January to December 2012. The station is a national meteorological site (Site ID: 59481) and is located in the Panyu district of Guangzhou, with an ele-

vation of 141 ma.s.l. (Fig. 1). Except for one highway, there are no major air pollutant emission sources within 500 m of GPACS. The site, being in the paths of major surface flows in the Pearl River Delta (PRD) region, is primarily influenced by the Southeast prevailing winds in the spring and summer and by the easterly prevailing winds in the autumn and winter (Wu et al., 2009). The site is a unique location for studying the air

²⁵ pollution of Guangzhou under different meteorological conditions (Deng et al., 2010).

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2.2 Monitoring equipment and measurement methods

PAN was measured with an online analyzer of gas chromatography coupled with electronic captured detector (GC-ECD, Meteorology Consult, Germany), which had been widely used in similar studies (Volz-Thomas et al., 2002; Zellweger, 2003; Zhang et al.,

- ⁵ 2009; Lin et al., 2011; J. B. Zhang et al., 2011; Lee et al., 2013; Zhang et al., 2014). The analyzer is a fully automated system consisting of a gas chromatography (GC) separation system, an electron capture detector (ECD), and a calibration unit. It is capable of 24 h real-time monitoring with a frequency of 6 measurements h⁻¹. Air samples were first pre-concentrated, then passed through a cooled capillary column to prevent
- thermal degradation of PAN during contact with the stationary phase, and finally were carried to the ECD with ultrapure nitrogen gas for quantitative analysis. A back-flushed precolumn prevented column contamination and reduced analysis run time. Sampling and chromatographic columns switch were controlled by a pneumatic 10-way valve. The data were processed with PC software Adam 32 (v1.44). Instrument detection limit was 50 pptv, with an accuracy about ±15 %.
- Two online monitors of gas chromatography coupled with flame ionization detector (GC-FID), GC5000VOC and GC5000BTX (AMA Instruments, Germany), were used to analyze 56 NMHCs designated as photochemical precursors by the United States Environment Protection Agency. The GC5000VOC was used for monitor-
- ²⁰ ing C₂–C₅ species and the GC5000BTX for C₆–C₁₂ species, both at a 1 h sampling frequency. Air samples were enriched in the GC5000VOC analyzer through two-stage trap, and then thermally desorbed when the temperature increased to 200 °C, followed by separation with two-dimensional chromatography. The chromatographic columns consisted of an Al₂O₃/Na₂SO₄ plot column (60 m × 0.32 mm inner diameter × 5 µm thickness) and a CARBOWAXTM back flushing column (30 m ×
- diameter × 5 μm thickness) and a CARBOWAX^{IM} back flushing column (30 m × 0.32 mm inner diameter × 0.25 μm thickness). The back flushing column was firstly used to remove the moisture component and high-boiling VOC species, and then the plot column was followed to separate the low-boiling VOC species. The GC5000BTX

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pre-concentrated the VOCs at 30°C and then thermally desorbed them at 270°C; afterwards, the analyzer separated the compounds in the DB-1 column ($60 \text{ m} \times 0.32 \text{ mm}$ inner diameter × 10 µm thickness), in order to achieve optimum separation and prevent interference from related compounds.

- O_3 was analyzed using an EC9810B ozone analyzer (Ecotech Co., Australia) based on the UV-absorption method and the Lambert–Beer Law. NO_x were measured by an EC9841B NO-NO₂-NO_x analyzer (Ecotech Co., Australia) with a heated Molybdenum NO₂ to NO converter and gas phase chemiluminescence technology was used to quantify NO concentrations. As the hot Molybdenum catalyst can also convert other
- odd-nitrogen (Winer et al., 1974), a particulate filter and a delay coil were applied between the sampling inlet and the catalyst to reduce the negative impact (Cao et al., 2013). We are aware that this method may still overestimate NO_x concentrations, so in the following sections, NO_x is denoted by NO_x^* when measured concentrations are described, and should be considered as the upper limits of their actual values (Dunlea
- et al., 2007; Ran et al., 2011). The O₃, NO, and NO₂ data were recorded with a data logger (Model 8816, Environmental Systems Corporation) in 1 min average. The conventional meteorological data (including UV solar radiation, temperature, wind speed, and wind direction) for the study period were made available through GPACS's regular monitoring and data collection; a detailed description of the station operation can be
 found in Lin et al. (2011). All instruments were housed in a quality controlled building to ensure normal running conditions.

2.3 QA/QC

The GC-ECD analyzer calibration was based on the method of producing PAN from photochemical reaction of NO standard gas, acetone (purity \geq 99.99%) and oxygen under ultraviolet light irradiation. The NO standard gas was (Foshan Kodi Gas Chemical Industry Co., LTD) prepared at 4.6 ppm level with a N₂ balance gas (purity \geq 99.9999%).

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The concentration of PAN was calculated using the following formula:

$$[\mathsf{PAN}] = \eta \cdot \frac{[\mathsf{NO}] \cdot Q_1}{Q_2} \cdot 10^3 \tag{1}$$

where [PAN] is the PAN concentration in ppbv; η is the yield of PAN production (93±5%); [NO] is the concentration of NO standard gas; Q_1 is the flow rate of NO

- standard gas (mLmin⁻¹); and Q_2 is the total flow rate after dilution (mLmin⁻¹). Before each experiment, the GC-ECD analyzer was calibrated using 5 point calibration method with a R^2 of 0.998, with regular one-point calibration weekly. Since the CCl₄ concentration in the air was very stable, its peak signal was used to check the stability of PAN signals.
- The GC-FID monitoring detector was calibrated monthly using mixed standard gases of NMHC species. The correlation coefficient ranged from 0.984 to 0.999, and the detection limits ranged from 0.03 to 0.09 ppbv. The O_3 generator within the EC9810B O_3 Analyzer was used for standard calibration and multipoint linearity calibration; the instrument detection limit was 0.05 ppbv.

15 2.4 HYSPLIT model

The HYSPLIT model was developed by the United States National Oceanic and Atmospheric Administration (NOAA) and Australia Bureau of Meteorology (Draxler and Hess, 1997). It is widely used for simulating the motion of air masses at the regional scale (Rappengluck et al., 2003; Zhang et al., 2009; Fischer et al., 2011; Zhang et al.,

2014). In this study, the meteorological data used in the model were derived from the global latitude–longitude projection (GBL) archive, with a 2.5° × 2.5° spatial resolution. To evaluate the influence of remote sources on the PAN concentration in Guangzhou, we examined the relationship between backward trajectories of air masses and PAN concentration at the study site.

3 Results and discussion

3.1 Concentrations of PAN and other photochemical pollutants

One finding of this study is that during the year-long observation both the concentrations of typical photochemical precursors and products were relatively high at the

- s study site (Fig. 2). The annual average concentrations of PAN and O_3 were 0.84 and 40.5 ppbv, respectively, while the annual average concentrations of NO_2 , NO, NO_x^* , and NMHCs were 31.2, 13.7, 44.9, and 38.1 ppbv, respectively. The hourly average PAN concentrations ranged from 0.07 to 12.0 ppbv, and there were 32 observation days in which the daily average concentration of PAN exceeded 5 ppbv health limit set
- ¹⁰ by WHO (1987). Our study also found that the daytime average PAN concentration in July of 2012 (0.95 ppbv) was higher than the level observed in the same month of 2006 (0.7 ppbv, Wang et al., 2010), indicating the worsening of PAN pollution in Guangzhou. Although PAN is not a target compound of routine air quality monitoring programs, due to its importance in photochemical processes, extensive observations have been
- carried out to measure its concentration in many environments. In Table 1, the annual average concentrations of PAN from this study are compared with those in other places around the world. It shows that the observed annual average concentration of PAN in Guangzhou (0.84 ppbv) are similar to the levels in Lanzhou (China), Los Angeles (US), and are notably higher than the levels in many other places.
- Figure 3 shows the monthly variations of PAN concentration, temperature, solar radiation, and relative humidity (RH) at GPACS for the study period. It can be seen that during the study period the PAN concentration was higher than its annual average concentration from August to October and lower from March to May. It is interesting to note that the highest monthly average concentration occurred in October but not in the sum-
- ²⁵ mer months (June to August) when the solar radiation was the strongest. It appears that although in the summer months the solar radiation was strong during the daytime, the temperatures remained high during the night, and therefore during the daytime the formation of PAN was favoured but during the night PAN readily underwent thermal 17101

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decomposition (Grosjean et al., 2002). In the fall season, the solar radiation was still relatively strong and temperature was relatively low, providing conditions that favour the PAN production and accumulation.

3.2 Concentration of PA radicals

- ⁵ To understand the observed concentrations of PAN and its potential sources, we have evaluated the rate constants of PAN production and thermal decomposition. In the process of PAN formation, the most important intermediate species is PA radicals, a key player in the photochemistry of the troposphere (Sehested et al., 1998). In this study, we did not measure the concentration of PA radicals. There is also no report of continu-
- ¹⁰ ous observation data of PA radicals for Guangzhou and surrounding areas. As a result, we estimated PA concentrations based on our PAN measurement data and relevant photochemical reaction constants. As Reactions (R2) and (R3) show, PAN is formed from the reaction of PA and NO₂, and at the same time PAN is also converted back to PA and NO₂ through thermal decomposition.

¹⁵
$$CH_3C(O)O_2NO_2 \rightarrow CH_3C(O)OO + NO_2$$

Because the concentrations of both PAN and NO_2 were measured during the study, we can use these reactions and their rate constants (Atkinson et al., 1997; Demore et al., 1997) to calculate the concentration of PA radicals when Reactions (R2) and (R3) were at equilibrium using Eq. (2).

²⁰ [PA] =
$$\frac{k_3[PAN]}{k_2[NO_2]}$$

where k_2 and k_3 are the rate constants for Reactions (R2) and (R3).

For PA calculations, observation data were selected from four days (5 and 6 May, 3 and 6 October) in May to October of 2012, the period of strong photochemical processes. In these four days, there were very little deposition process and the wind

(2)

(R3)

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speeds were less 2 m s^{-1} , suggesting a weak impact of meteorological conditions relative to chemical processes. The PA concentrations were calculated according to Eq. (2), and the results are shown in Fig. 4.

It can be seen that the estimated concentration of PA radicals were high during the daytime but low during the night. This is consistent with the knowledge that PA radicals are primarily derived from photochemical reactions. The hourly average concentrations of PA radicals for the four days are 0.031, 0.04, 0.065, and 0.15 pptv. A comparison

(Table 2) shows that the calculated PA radical levels in Guangzhou for the study period are much higher than those in many other places, indicating strong photochemical
 oxidation processes in Guangzhou area. Since PA radicals are primarily produced by photochemical reactions (LaFranchi et al., 2009; Liu et al., 2010), high concentrations

of PA radicals were likely a result of the high concentrations of VOCs in Guangzhou. The PA concentrations estimated above can be affected by the uncertainties asso-

ciated with NO₂ and PAN measurements. The uncertainty for NO₂ measurement normally is around 7 % (Cao et al., 2013), and that for PAN is only about 5 %. Combined, the uncertainties from the NO₂ and PAN measurements would introduce an error of approximately 10 % for the estimated PA concentration. Therefore, the uncertainty in estimating PA should be acceptable for the purpose of this work.

The rate of PAN production can be calculated as follows:

$${}_{20} \quad \frac{d[PAN]}{dt} = k_2[CH_3C(O)OO][NO_2]$$
(3)

and similarly the thermal decomposition rate of PAN can be calculated as:

$$\frac{d[PAN]}{dt} = k_3[PAN]$$

(4)

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Therefore, based on the estimated concentration of PA radicals and other observation data, we can obtain the rate of production and the rate of thermal decomposition for PAN at an article and the second data at the second

PAN at specific conditions. From Fig. 4, it is clear that PAN formation mainly occurred 17103

between 08:00-18:00 LT, and thus for the selected four observation days, we used data from this period for our analysis. Our calculations show that for this time period, the rate of PAN production for the four days are 0.08, 0.09, 0.28, and 0.61 ppbv 10 min^{-1} , while the rate of thermal decomposition are 0.13, 0.16, 0.63, and 1.09 ppbv 10 min^{-1} . Clearly,

- the rate of thermal decomposition of PAN is greater than the rate of its production. One major factor for this could be the high temperatures at the study site during those four days, with the temperatures averaging 26.8±2.4, 27.2±2.2, 28.1±3.0, and 29.3±2.6 °C. High temperatures promote the decomposition of PAN and reduce its accumulation in the atmosphere. However, even under such conditions, the concentrations of PAN
- observed during the four days were still significantly high, suggesting the contributions of PAN from sources beyond the local photochemical processes. Using Eqs. (3) and (4), we calculated the monthly PAN production and decomposition

under the equilibrium condition for the photochemical reactions for the period between 08:00–18:00 LT, and the results are shown in Fig. 5. As can be seen from Fig. 5, PAN

production is high for August, September, and October, but the decomposition is also fairly high for these months. Since during photochemical reactions the PAN production and decomposition occur at the same time, the difference between the two is then the net increase of PAN concentration.

By comparing this net increase to the measured PAN concentration, we can estimate the contribution of PAN transported to the study site from distant sources, as shown in Fig. 6. The calculations suggest that for the entire year of 2012, PAN from distant

sources accounts for about 30% of the total measured PAN at the study site. The PAN contributions by distant sources are different among individual months, with the highest contributions for the months in the fall (56%) and the lowest for the months of the summer (0%)

3.3 Sources of PAN in Guangzhou

3.3.1 Contributions of NMHCs to PAN production

Reactions (R1a) and (R1b) indicate that NMHCs are key precursors that produce PA radicals. However, contributions of specific NMHCs to the formation of PAN in the atmo-

- sphere are not well understood, particularly in an environment characterized by strong emissions of NMHCs, such as in Guangzhou. Knowledge about the relative contributions of individual NMHC species to PAN formation can help identify sources of PAN and provide valuable information for developing control measures.
- Table 3 lists the annual average concentrations of 56 NMHC species measured in this study and their ability to form three key precursors for PAN (acetaldehyde, acetone, and MGLYOX). A total of 14 alkanes, 8 alkenes, and 3 aromatics meet the criteria. We calculated the relative contributions of these 24 NMHCs to PAN formation using MCM (MCMv3.1, Master Chemical Mechanism) (Bloss et al., 2005; Michael et al., 1997; Jenkin et al., 2003; Saunders et al., 2003), and the results are shown in Table 4. Table 4
- ¹⁵ indicates that among the three NMHC groups, alkenes are the largest contributor to PAN production, accounting for 53% of the total, and aromatics and alkanes account for 11 and < 7%, respectively.</p>

The calculated relative contributions of individual NMHCs to PAN production are markedly different. The big contributors include isoprene, cis-2-pentene, m-&p-xylenes,

and toluene, among the others. The contribution by isoprene alone is about 29% (or as high as 41% of the total contributions by all 56 NMHCs), consistent with the calculations of other studies (Fischer et al., 2014; Folberth et al., 2006; Horowitz et al., 1998).

It should be noted that in this study, the observed PAN concentration (0.84 ppbv) is about 1.4 times higher than the calculated value (0.60 ppbv, Table 4). This suggests that there might be additional contributions to the PAN formation from other NMHCs that were not captured in our measurement. There are also the potential contributions to the PAN observed at the study site from distant sources.

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3.3.2 Impact of distant sources on PAN concentrations in Guangzhou

Relationships among PAN and other photochemical pollutants

In order to understand the sources of PAN, we performed a Pearson correlation analysis to examine the relationships among PAN, O_3 , NO_x^* , and NMHCs (Table 5). The results of this analysis indicate that there is a modest correlation between O_3 and PAN. This is different from the findings of several other studies (Tsani-Bazaca et al.,

- 1988; Gaffney et al., 1999; Beine et al., 2000; Zhang et al., 2009). The lack of correlation between PAN and O_3 at the study site suggests that during our study period, the concentrations of PAN and O_3 were influenced by sources or processes besides
- the photochemical reactions of precursors. We have observed that at the study site the O₃ concentration showed a clear single peak diurnal variation pattern, indicating that it was primarily produced from local photochemical reactions, which is consistent with the conclusion of Y. N. Zhang et al. (2011). Thus, PAN and O₃ in Guangzhou do not share similar characteristics and likely are influenced by the distant sources differently.
 This is consistent with the results of our earlier calculations, which shows that about
- 30 % of the PAN observed at the study site is from outside sources. NO₂ plays an important role in the formation of PAN, and in many places a positive correlation between the two species has been well documented (e.g., Lee et al., 2013; Zhang et al., 2014). However, in our study a modest correlation between PAN and NO₂
- was found, with correlation coefficients of 0.262, 0.042, -0.241, and -0.160 for the daytime in four seasons. This supports the notion that a significant portion of the PAN observed at the study site was formed in other places and subsequently transported to the Guangzhou area. In addition, the average NMHCs / NO_x ratio found in our study was 5.1, lower than the levels found in other places (Hernandez and Ortiz, 1999; Rubio
- et al., 2005). This further suggests that non-local sources were partially responsible for the high PAN levels observed at the study site.

Transport of PAN from potential distant sources

In our earlier discussions, based on measurement data and calculations, we have suggested that some of the PAN in Guangzhou came from non-local sources, likely through atmospheric transport. We have back calculated the air mass trajectories for

all the months of the observation period using HYSPLIT (Version 4.9, Draxler and Hess, 1997). The meteorological data used for calculations were obtained from NOAA (24 h). The calculation results are presented in Fig. 7.

Figure 7 shows that during March, April, May, and July, air masses moved from ocean to the study site, bringing in clean air. In October, air masses came from indus-

trialized cities Dongguan and Shenzhen (see Fig. 1), transporting a large amount of air pollutants and causing high levels of PAN at the study site. In December, air masses first passed heavily polluted Foshan area before arriving at the study site and, with the mild temperatures during the month, resulting in relatively high PAN levels. Similarly, in September air masses also passed through heavily polluted Shenzhen, causing high levels of PAN.

Although the air mass trajectories for November are similar to those for October, the PAN levels in November were much lower than the levels in October. Meteorological data show that four cold air masses passed through the study site on 13, 16, 23, and 26 November, and this may have considerably reduced amount of PAN transported to

• the study site. Nevertheless, the PAN levels in November were still comparable to the levels in the summer months when the solar radiation was strong.

Clearly, regional transport of air pollutants has a strong impact on the PAN concentrations in Guangzhou, especially when the air masses pass through highly industrialized cities of Dongguan and Shenzhen. Because of the contributions of PAN from distant

²⁵ sources, correlations between major photochemical pollutants PAN, O₃, and NO₂ found at many other places were not observed in Guangzhou.

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4 Conclusions

The concentrations of PAN, O_3 , NO_x , and NMHCs were continuously monitored from January to December 2012, at an atmospheric composition station in Guangzhou, China. Based on the observation data, we examined the relationship between PAN and other key photochemical precursors and products, and investigated the different

sources of PAN in Guangzhou.

During the study period, the maximum hourly average concentrations of PAN and O_3 were 1.86 and 52.8 ppbv, respectively. When compared to historical data, the concentrations of PAN and O_3 in Guangzhou area seemed to show a continued increase, contributing to an increasingly strong oxidation atmospheric environment.

NMHCs play an important role in the production of PAN in Guangzhou but their contributions to this process vary with species. During the study, the dominant contributors to the production of PAN were alkenes, with about 53% of the estimated total contribution from these species. Aromatics were also important, with around 11% of the total contribution. Alkanes contributed the least, accounting for < 10% of the total.

The atmospheric environment of Guangzhou was not only impacted by photochemical processes but also by the pollutants transported to the area by air masses from the heavily industrialized cities of Dongguan and Shenzhen. This is supported by the observation that the measured PAN concentrations are higher than the concentrations

²⁰ calculated from photochemical reactions of precursors. Future work will be focused on the compositions of air masses from the areas surrounding Guangzhou.

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Altshuller, A. P.: PANs in the atmosphere, J. Air Waste Manage., 43, 1221–1230, 1993.
Aneja, V. P., Hartsell, B. E., Kim, D. S., and Grosjean, D.: Peroxyacetyl nitrate in Atlanta, Georgia: comparison and analysis of ambient data for suburban and downtown locations, J. Air Waste Manage., 49, 177–184, 1999.

Atkinson, R.: Gas-phase tropospheric chemistry of organic compounds: a review, Atmos. Environ., 41, S200–S240, 2007.

Beine, H. J. and Krognes, T.: The seasonal cycle of peroxyacetyl nitrate (PAN) in the Arctic, Atmos. Environ., 34, 933–940, 2000.

Bertram, T. H., Perring, A. E., Wooldridge, P. J., Dibb, J., Avery, M. A., and Cohen, R. C.: On the export of reactive nitrogen from Asia: NO_x partitioning and effects on ozone, Atmos. Chem. Phys., 13, 4617–4630, doi:10.5194/acp-13-4617-2013, 2013.

Bloss, C., Wagner, V., Bonzanini, A., Jenkin, M. E., Wirtz, K., Martin-Reviejo, M., and Pilling, M. J.: Evaluation of detailed aromatic mechanisms (MCMv3 and MCMv3.1) against
 ¹⁵ environmental chamber data, Atmos. Chem. Phys., 5, 623–639, doi:10.5194/acp-5-623-2005. 2005.

- Bottenheim, J. W., Sirios, A., Brice, K. A., and Gallant, A. J.: Five years of continuous observations of PAN and ozone at a rural location in eastern Canada, J. Geophys. Res., 99, 5333–5352, 1994.
- 20 Cao, W., Zeng, L., Wu, Y., and Hu, M.: An comparative analysis of the accuracy of atmospheric NO_x measurements, Acta Scientiae Circumstantiae, 33, 346–355, 2013.
 - Cleary, P. A., Wooldridge, P. J., Millet, D. B., McKay, M., Goldstein, A. H., and Cohen, R. C.: Observations of total peroxy nitrates and aldehydes: measurement interpretation and inference of OH radical concentrations, Atmos. Chem. Phys., 7, 1947–1960, doi:10.5194/acp-7-1947-2007, 2007.

Crutzen, P. J.: The role of NO and NO₂ in the chemistry of the troposphere and the stratosphere, Annu. Rev. Earth Pl. Sc., 7, 443–472, 1979.

Demore, W. B., Sander, S. P., Golden, D. M., Hampson, R. F., Kurylo, M. J., and Howard, C. J.: Chemical kinetics and photochemical data for use in stratospheric modelling, JPL Publication, 97–4, 1–266, 1997.

Deng, X. J., Wang, X. M., and Zhao, C. S.: The typical process average concentrations of VOCs and chemical reactivity in the PRD, J. Environ. Sci.-China., 30, 1153–1161, 2010.

- Derwent, R. G. and Jenkin, M. E.: Hydrocarbons and the long-range transport of ozone and PAN across Europe, Atmos. Environ., 25, 1661–1678, 1991.
- Dodge, M. C.: Combined use of modeling techniques and smog chamber data to derive ozone precursor relationships, in: Proceedings of the International Conference on Photochemical
- Oxidant Pollution and its Control, Vol. II, EPA-600/3-77-0016, edited by: Dimitriades, B., US EPA, RTP, NC, 881–889, 1977.
 - Draxler, R. R. and Hess, G. D.: Description of the HYSPLIT 4 modeling system, NOAA Technical Memorandum, ERL ARL–224, NOAA Air Resources Laboratory, Silver Spring, MD, 24, 1997.
- Dunlea, E. J., Herndon, S. C., Nelson, D. D., Volkamer, R. M., San Martini, F., Sheehy, P. M., Zahniser, M. S., Shorter, J. H., Wormhoudt, J. C., Lamb, B. K., Allwine, E. J., Gaffney, J. S., Marley, N. A., Grutter, M., Marquez, C., Blanco, S., Cardenas, B., Retama, A., Ramos Villegas, C. R., Kolb, C. E., Molina, L. T., and Molina, M. J.: Evaluation of nitrogen dioxide chemiluminescence monitors in a polluted urban environment, Atmos. Chem. Phys., 7, 2691–2704, doi:10.5194/acp-7-2691-2007, 2007.
- Fadnavis, S., Schultz, M. G., Semeniuk, K., Mahajan, A. S., Pozzoli, L., Sonbawne, S., Ghude, S. D., Kiefer, M., and Eckert, E.: Trends in peroxyacetyl nitrate (PAN) in the upper troposphere and lower stratosphere over southern Asia during the summer monsoon season: regional impacts, Atmos. Chem. Phys., 14, 12725–12743, doi:10.5194/acp-14-12725-2014, 2014.
 - Fischer, E. V., Jaffe, D. A., and Weatherhead, E. C.: Free tropospheric peroxyacetyl nitrate (PAN) and ozone at Mount Bachelor: potential causes of variability and timescale for trend detection, Atmos. Chem. Phys., 11, 5641–5654, doi:10.5194/acp-11-5641-2011, 2011.
 Fischer, E. V., Jacob, D. J., Yantosca, R. M., Sulprizio, M. P., Millet, D. B., Mao, J., Paulot, F.,
- Singh, H. B., Roiger, A., Ries, L., Talbot, R.W., Dzepina, K., and Pandey Deolal, S.: Atmospheric peroxyacetyl nitrate (PAN): a global budget and source attribution, Atmos. Chem. Phys., 14, 2679–2698, doi:10.5194/acp-14-2679-2014, 2014.
- Folberth, G. A., Hauglustaine, D. A., Lathière, J., and Brocheton, F.: Interactive chemistry in the Laboratoire de Météorologie Dynamique general circulation model: model description and
- ³⁰ impact analysis of biogenic hydrocarbons on tropospheric chemistry, Atmos. Chem. Phys., 6, 2273–2319, doi:10.5194/acp-6-2273-2006, 2006.

Discussion Paper

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Discussion Paper

Discussion Paper

Discussion Paper

Discussion Paper

- Gaffney, J. S., Marley, N. A., and Prestbo, E. W.: Measurement of peroxyacetyl nitrate at a remote site in the southwestern Unite States: tropospheric implication, Environ. Sci. Technol., 27, 1905–1910, 1993.
- Gaffney, J., Marley, N. A., Steele, H. D., Drayton, P. J., and Hubbe, J. M.: Aircraft measurements of nitrogen dioxide and peroxyacyl nitrates using luminol chemiluminescence with fast capillary gas chromatography, Environ. Sci. Technol., 33, 3285–3289, 1999.
- Glavas, S. and Moschonas, N.: Determination of PAN, PPN, PnBN and selected pentyl nitrates in Athens, Greece, Atmos. Environ., 35, 5467–5475, 2001.
- Goulding, K. W. T., Bailey, N. J., Bradbury, N. J., Hargreaves, P., Howe, M., Murphy, D. V.,
 Poulton, P. R., and Willison, T. W.: Nitrogen deposition and its contribution to nitrogen cycling and associated soil processes, New Phytol., 139, 49–58, 1998.
 - Grosjean, E., Grosjean, D., Woodhouse, L. F., and Yang, Y. J.: Peroxyacetyl nitrate and peroxypropionyl nitrate in Porto Alegre, Brazil, Atmos. Environ., 36, 2405–2419, 2002.
- Hernández, F. and Ortiz, E.: Application of photochemical trajectory model to evaluate ozone
 formation by atmospheric concentrations and emissions of propane and butane in Mexico
 City Metropolitan zone, Mol. Eng., 8, 447–458, 1999.
 - Horowitz, L. W., Liang, J. Y., Gardner, G. M., and Jacob, D. J.: Export of reactive nitrogen from North America during summertime: sensitivity to hydrocarbon chemistry, J. Geophys. Res., 103, 13451–13476, 1998.
- ²⁰ Hudman, R. C., Jacob, D. J., Cooper, O. R., Evans, M. J., Heald, C. L., Park, R. J., Fehsenfeld, F., Flocke, F., Holloway, J., Hubler, G., Kita, K., Koike, M., Kondo, Y., Neuman, A., Nowak, J., Oltmans, S., Parrish, D., Roberts, J. M., and Ryerson, T.: Ozone production in transpacific Asian pollution plumes and implications for ozone air quality in California, J. Geophys. Res., 109, 1–14, 2004.
- Jacobi, H. W. and Schrems, O.: Peroxyacetyl nitrate (PAN) distribution over the South Atlantic Ocean, Phys. Chem., 1, 5517–5521, 1999.
 - Jacobi, H. W., Weller, R., Bluszcz, T., and Schrems, O.: Latitudinal distribution of peroxyacetyl nitrate (PAN) over the Atlantic Ocean, J. Geophys. Res., 104, 26901–26912, 1999.
- Jenkin, M. E. and Clemitshaw, K. C.: Ozone and other secondary photochemical pollutants: chemical processes governing their formation in the planetary boundary layer, Atmos. Environ., 34, 2499–2527, 2000.

- Jenkin, M. E., Saunders, S. M., and Pilling, M. J.: The tropospheric degradation of volatile organic compounds: a protocol for mechanism development, Atmos. Environ., 31, 81–104, 1997.
- Jenkin, M. E., Saunders, S. M., Wagner, V., and Pilling, M. J.: Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part B): tropospheric degradation of aromatic volatile organic compounds, Atmos. Chem. Phys., 3, 181–193, doi:10.5194/acp-3-181-2003,
 - 2003. Kleindienst, T. E.: Recent developments in the chemistry and biology of peroxyacetyl nitrate,
 - Res. Chem. Intermediat., 20, 335–384, 1994.
- Kourtidis, K. A., Fabian, P., Zerefos, C., Rappengluck, B.: Peroxyacetyl nitrate (PAN), peroxypropionyl nitrate (PPN) and PAN/ozone ratio measurements at three sites in Germany, Tellus B, 45, 442–457, 1993.
 - LaFranchi, B. W., Wolfe, G. M., Thornton, J. A., Harrold, S. A., Browne, E. C., Min, K. E., Wooldridge, P. J., Gilman, J. B., Kuster, W. C., Goldan, P. D., de Gouw, J. A., McKay, M.,
- Goldstein, A. H., Ren, X., Mao, J., and Cohen, R. C.: Closing the peroxy acetyl nitrate budget: observations of acyl peroxy nitrates (PAN, PPN, and MPAN) during BEARPEX 2007, Atmos. Chem. Phys., 9, 7623–7641, doi:10.5194/acp-9-7623-2009, 2009.
 - Lee, G., Jang, Y., Lee, H., Han, J. S., Kim, K. R., and Lee, M.: Characteristic behavior of peroxyacetyl nitrate (PAN) in Seoul megacity, Korea, Chemosphere, 73, 619–628, 2008.
- Lee, G. W., Soon, C. H., Lee, T. Y., Soon, C. J., Su, P. J., and Young, A. J.: Variations of regional background peroxyacetyl nitrate in marine boundary layer over Baengyeong Island, South Korea, Atmos. Environ., 61, 533–541, 2012.
- Lee, J. B., Yoon, J. S., Jung, K., Eom, S. W., Chae, Y. Z., Ju, C. S., Kim, D. S., Sohn, J. R., and Kim, K. H.: Peroxyacetyl nitrate (PAN) in the urban atmosphere, Chemosphere, 93, 1796– 1803, 2013.
- Lin, W., Xu, X., Ge, B., and Liu, X.: Gaseous pollutants in Beijing urban area during the heating period 2007–2008: variability, sources, meteorological, and chemical impacts, Atmos. Chem. Phys., 11, 8157–8170, doi:10.5194/acp-11-8157-2011, 2011.
- Liu, H., Wang, X. M., Zhang, J. P., He, K. B., Wu, Y., and Xu, J. Y.: Emission controls and changes in air quality in Guangzhou during the Asian Games, Atmos. Environ., 76, 81–93, 2013.

Discussion Paper

Discussion Paper

Discussion Paper

Discussion Paper

- Liu, Z., Wang, Y. H., Gu, D., Zhao, C., Huey, L. G., and Stickel, R.: Evidence of reactive aromatics as a major source of peroxyacetyl nitrate over China, Environ. Sci. Technol., 44, 7017– 7022, 2010.
- Magnani, F., Mencuccini, M., Borghetti, M., Berbigier, P., Berninger, F., Delzon, S., Grelle, A., Hari, P., Jarvis, P. G., Kolari, P., Kowalski, A. S., Lankreijer, H., Law, B. E., Lindroth, A., Lous-
- tau, D., Manca, G., Moncrieff, J. B., Rayment, M., Tedeschi, V., Valentini, R., and Grace, J.: The human footprint in the carbon cycle of temperate and boreal forests, Nature, 447, 848– 850, 2007.
- Marley, N. A., Gaffney, J. S., Ramos-Villegas, R., and Cárdenas González, B.: Compari-
- son of measurements of peroxyacyl nitrates and primary carbonaceous aerosol concentrations in Mexico City determined in 1997 and 2003, Atmos. Chem. Phys., 7, 2277–2285, doi:10.5194/acp-7-2277-2007, 2007.
 - McFadyen, G. G. and Cape, J. N.: Peroxyacetyl nitrate in eastern Scotland, Sci. Total Environ., 337, 213–222, 2005.
- Mills, G. P., Sturges, W. T., Salmon, R. A., Bauguitte, S. J.-B., Read, K. A., and Bandy, B. J.: Seasonal variation of peroxyacetylnitrate (PAN) in coastal Antarctica measured with a new instrument for the detection of sub-part per trillion mixing ratios of PAN, Atmos. Chem. Phys., 7, 4589–4599, doi:10.5194/acp-7-4589-2007, 2007.

Moore, D. P. and Remedios, J. J.: Seasonality of Peroxyacetyl nitrate (PAN) in the upper troposphere and lower stratosphere using the MIPAS-E instrument, Atmos. Chem. Phys., 10, 6117–6128, doi:10.5194/acp-10-6117-2010, 2010.

Movassaghi, K., Russo, M, V., and Avino, P.: The determination and role of peroxyacetil nitrate in photochemical processes in atmosphere, J. Chem. Cen., 6, S8, 2012.

- Nielsen, T., Samuelsson, U., Grennfelt, C., and Thomsen, E. L.: Peroxyacetyl nitrate in long range transported polluted air, Nature, 293, 553–555, 1981.
- Pandey Deolal, S., Henne, S., Ries, L., Gilge, S., Weers, U., Steinbacher, M., Staehelin, J., and Peter, T.: Analysis of elevated springtime levels of Peroxyacetyl nitrate (PAN) at the high Alpine research sites Jungfraujoch and Zugspitze, Atmos. Chem. Phys., 14, 12553–12571, doi:10.5194/acp-14-12553-2014, 2014.
- Pitts, J. N., Doyle, G. J., and Lloyd, A. C.: Chemical Transformations in Photochemical Smog and Their Applications to Air Pollution Control Strategies, NSF-RANN Grant No. ENV73-02904-A03, First Annual Progress Report, 1975.

- Pollack, I. B., Ryerson, T. B., Trainer, M., Neuman, J. A., Roberts, J. M., and Parrish, D.: Trends in ozone, its precursors, and related secondary oxidation products in Los Angeles, California: a synthesis of measurements from 1960 to 2010, J. Geophys. Res., 118, 5893–5911, doi:10.1002/jgrd.50472, 2013.
- ⁵ Qin, Y., Tonnesen, G. S., and Wang, Z.: Weekend/weekday differences of ozone, NO_x, CO, VOCs, PM₁₀ and the light scatter during ozone season in southern California, Atmos. Environ., 38, 3069–3087, 2004.
 - Ran, L., Zhao, C. S., Xu, W. Y., Lu, X. Q., Han, M., Lin, W. L., Yan, P., Xu, X. B., Deng, Z. Z., Ma, N., Liu, P. F., Yu, J., Liang, W. D., and Chen, L. L.: VOC reactivity and its effect on
 - ozone production during the HaChi summer campaign, Atmos. Chem. Phys., 11, 4657–4667, doi:10.5194/acp-11-4657-2011, 2011.
 - Rappenglück, B., Melas, D., and Fabian, P.: Evidence of the impact of urban plumes on remote sites in the Eastern Mediterranean, Atmos. Environ., 37, 1853–1864, 2003.
- Ridley, B. A., Shetter, J. D., Walega, J. G., Madronich, S., Elsworth, C. M., Grahek, F. E.,
 Fehsenfeld, F. C., Norton, R. B., Parrish, D. D., Huebler, G., Buhr, M., Williams, E. J., All wine, E. J., and Westberg, H. H.: The behavior of some organic nitrates at Boulder and
 Niwot Ridge, Colorado, J. Geophys. Res., 95, 13949–13961, 1990.
 - Roberts, J. M.: PAN and related compounds, in: Volatile Organic Compounds in the Atmosphere, Blackwell Publishing Ltd, 221–268, 2007.
- Roberts, J. M., Tanner, R. L., Newman, L., Bowersox, V. C., Bottenheim, J. W., Anlauf, K. G., Brice, K. A., Parrish, D. D., Fehsenfeld, F. C., Buhr, M. P., Meagher, J. F., and Bailey, E. M.: Relationships between PAN and ozone at sites in eastern North America, J. Geophys. Res., 100, 22821–22830, doi:10.1029/95jd01221, 1995.
- Roberts, J. M., Stroud, C. A., Jobson, B. T., Trainer, M., Hereid, D., Williams, E., Fehsenfeld, F.,
 Brune, W., Martinez, M., and Harder, H.: Application of a sequential reaction model to PANs and aldehyde measurements in two urban areas, Geophys. Res. Lett., 28, 4583–4586, 2001.
- Roberts, J. M., Flocke, F., Stroud, C. A., Hereid, D., Williams, E., Fehsenfeld, F., Brune, W., Martinez, M., and Harder, H.: Ground-based measurements of peroxycarboxylic nitric anhydrides (PANs) during the 1999 Southern Oxidants Study Nashville Intensive, J. Geophys.
 Res., 107, 4554, doi:10.1029/2001JD000947, 2002.
- Roberts, J. M., Marchewka, M., Bertman, S. B., Goldan, P., Kuster, W., de Gouw, J., Warneke, C., Williams, E., Lerner, B., Murphy, P., Apel, E., and Fehsenfeld, F. C.: Analysis of

- Roberts, J. M., Marchewka, M., Bertman, S. B., Sommariva, R., Warneke, C., de Gouw, J., Kuster, W., Goldan, P., Williams, E., Lerner, B. M., Murphy, P., and Fehsenfeld, F. C.: Measurements of PANs during the New England Air Quality Study 2002, J. Geophys. Res., 112,
- 1–14, 2007. Rolph, G.: Real-time environmental applications and display system (ready), available at: http: //www.arl.noaa.gov/ready/hysplit4.html (last access: 17 June 2015), NOAA Air Resources Laboratory, Silver Spring, MD, 2003.
- Rubio, M. A., Gramsch, E., and Villena, E. L. G.: Seasonal dependence of peroxyacetyl nitrate (PAN) concentrations in downtown Santiago, Chile, Atmosfera, 20, 319–328, 2007.
- Saunders, S. M., Jenkin, M. E., Derwent, R. G., and Pilling, M. J.: Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of non-aromatic volatile organic compounds, Atmos. Chem. Phys., 3, 161–180, doi:10.5194/acp-3-161-2003, 2003.
- Schrimpf, W., Lienaerts, K., Muller, K. P., Rudolph, J., Neubert, R., and Schubler, W.: Dry deposition of peroxyacetyl nitrate (PAN): determination of its deposition velocity at night from measurements of the atmospheric PAN and 222 Radon concentration gradient, Geophys. Res. Lett., 23, 3599–3602, 1996.

15

- ²⁰ Sehested, J., Christensen, L. K., Møgelberg, O. J., Nielsen, O. J., Wallingon, T. J., and Guschin, A.: Absolute and relative rate constants for thereactions $CH_3C(O)O_2 + NO$ and $CH_3C(O)O_2 + NO_2$ and thermal stability of $CH_3C(O)O_2NO_2$, J. Phys. Chem., 102, 1779–1789, 1998.
 - Sillman, S. and Samson, P. J.: The impact of temperature on oxidant formation in urban, polluted rural and remote environments, J. Geophys. Res., 100, 11497–11508, 1995.
- Singh, H. B.: Reactive nitrogen in the troposphere, Environ. Sci. Technol., 21, 320–327, 1987.
 Singh, H. B. and Hanst, P. L.: Peroxyacetyl nitrate (PAN) in the unpolluted atmosphere: an important reservoir for nitrogen oxides, Geophys. Res. Lett., 8, 941–944, 1981.
 Singh, H. B. and Salas, L. J.: Measurements of peroxyacetyl nitrate (PAN) and peroxypropionyl

nitrate (PPN) at selected urban, rural and remote sites, Atmos. Environ., 23, 231–238, 1989.

Sparks, J. P., Roberts, J. M., and Monson, R. K.: The uptake of gaseous organic nitrogen by leaves: a significant global nitrogen transfer process, Geophys. Res. Lett., 30, 2189, doi:10.1029/2003GL018578, 2003.

Spicer, C. W.: Nitrogen oxide reactions in the urbane plume of Boston, Science, 5, 1095–1097, 1982.

- Stephens, E. R. and Nasim, A.: Absorptivities for infrared determination of peroxyacyl nitrates, Anal. Chem., 36, 928–929, 1964.
- Sun, E. J. and Huang, M. H.: Detection of peroxyacetyl nitrate phytotoxic level and its effects on vegetation in Taiwan, Atmos. Environ., 29, 2899–2904, 1995.
 - Talukdar, R. K., Burkholder, J. B., Schmoltner, A. M., Roberts, J. M., Wilson, R. R., and Ravishankara, A. R.: Investigation of the loss processes for peroxyacetyl nitrate in the atmosphere: UV photolysis and reaction with OH, J. Geophys. Res., 100, 14163–14173, 1995.
- Tanimoto, H., Furutani, H., Kato, S., Matsumoto, J., Makide, Y., Akimoto, H.: Seasonal cycles of ozone and oxidize nitrogen species in northeast Asia 1. Impact of regional climatology and photochemistry observed during RISOTTO 1999–2000, J. Geophys. Res., 107, 4747, doi:10.1029/2001JD001496, 2002.
 - Taylor, O. C.: Importance of peroxyacetyl nitrate (PAN) as a phytotoxic air pollutant, J. Air Pollut. Contr. Assoc., 19, 347–351, 1969.
- Tereszchuk, K. A., Moore, D. P., Harrison, J. J., Boone, C. D., Park, M., Remedios, J. J., Randel, W. J., and Bernath, P. F.: Observations of peroxyacetyl nitrate (PAN) in the upper troposphere by the Atmospheric Chemistry Experiment-Fourier Transform Spectrometer (ACE-FTS), Atmos. Chem. Phys., 13, 5601–5613, doi:10.5194/acp-13-5601-2013, 2013.
- ²⁰ Tsani-Bazaca, E., Glavas, S., and Güsten, H.: Peroxyacetyl nitrate (PAN) concentrations in Athens, Greece, Atmos. Environ., 22, 2283–2286, 1988.
 - Tuazon, E. C., Carter, W. P. L., and Atkinson, R.: Thermal decomposition of peroxyacetyl nitrate and reactions of acetyl peroxy radicals with NO and NO₂ over the temperature range 283– 313 K, J. Phys. Chem., 95, 2434–2437, 1991.
- Volz-Thomas, A., Xueref, I., and Schmitt, R.: Automatic gas chromatograph and calibration system for ambient measurements of PAN and PPN, Environ. Sci. Pollut. R., 9, 72–76, 2002.
 - Wang, B., Shao, M., Roberts, J. M., Yang, G., Yang, F., and Hu, M.: Ground-based on-line measurements of peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN) in the Pearl River Delta, China, Int. J. Environ. An. Ch., 90, 548–559, 2010.
- Watanabe, I., Nakanishi, M., Tomita, J., Hatakeyama, S., Murano, K., Mukai, H., and Bandou, H.: Atmospheric peroxyacetyl nitrate in urban/remote sites and the lower troposphere around Japan, Environ. Pollut., 102, 253–261, 1998.

Discussion Paper

- Whalley, L. K., Lewis, A. C., McQuaid, J. B., Purvis, R. M., Lee, J. D., Stemmler, K., Zellweger, C., and Ridgeon, P.: Two high-speed, portable GC systems designed for the measurement of non-methane hydrocarbons and PAN: results from the Jungfraujoch High Altitude Observatory, J. Environ. Monitor., 6, 234-241, 2004.
- WHO: Air Quality Guidelines for Europe, WHO Regional Office in Europe, Copenhagen, 1987. Williams II, E. L. and Grosjean, D.: Southern California air quality study: peroxyacetyl nitrate, Atmos. Environ., 24A, 2369-2377, 1990.
- Winer, A. M., Peters, J. W., Smith, J. P., and Pitts, J. N.: Response of commercial chemiluminescent nitric oxide-nitrogen dioxide analyzers to other nitrogen-containing compounds, Environ. Sci. Technol., 8, 1118–1121, 1974.
- Wolfe, G. M., Thornton, J. A., McNeill, V. F., Jaffe, D. A., Reidmiller, D., Chand, D., Smith, J., Swartzendruber, P., Flocke, F., and Zheng, W.: Influence of trans-Pacific pollution transport on acyl peroxy nitrate abundances and speciation at Mount Bachelor Observatory during INTEX-B, Atmos. Chem. Phys., 7, 5309–5325, doi:10.5194/acp-7-5309-2007, 2007.

10

- Wolfe, G. M., Thornton, J. A., Yatavelli, R. L. N., McKay, M., Goldstein, A. H., LaFranchi, B., Min, K.-E., and Cohen, R. C.: Eddy covariance fluxes of acyl peroxy nitrates (PAN, PPN and MPAN) above a Ponderosa pine forest, Atmos. Chem. Phys., 9, 615-634, doi:10.5194/acp-9-615-2009, 2009,
- Wu, D., Mao, J. T., Deng, X. J., Tie, X. X., Li, F., Tan, H. B., and Bi, X. Y.: The radiation characteristics of black carbon aerosols in observational studies in Pearl River Delta, Sci. China 20
 - Ser. D, 39, 1542-1553, 2009. Wunderli, S. and Gehrig, R.: Influence of temperature on formation and stability of surface PAN
 - and ozone: a two year field study in Switzerland, Atmos. Environ., 25A, 1599-1608, 1991. Zellweger, C., Forrer, J., Hofer, P., Nyeki, S., Schwarzenbach, B., Weingartner, E., Ammann, M.,
- and Baltensperger, U.: Partitioning of reactive nitrogen (NO_{ν}) and dependence on me-25 teorological conditions in the lower free troposphere, Atmos. Chem. Phys., 3, 779-796, doi:10.5194/acp-3-779-2003, 2003.
 - Zhang, H. L., Xu, X. B., Lin, W. L., and Wang, Y.: Wintertime peroxyacetyl nitrate (PAN) in the megacity Beijing: the role of photochemical and meteorological processes, J. Environ. Sci., 26, 83-96, 2014.
- Zhang, J. B., Xu, Z., Yang, G., and Wang, B.: Peroxyacetyl nitrate (PAN) and peroxypropionyl nitrate (PPN) in urban and suburban atmospheres of Beijing, China, Atmos. Chem. Phys. Discuss., 11, 8173-8206, doi:10.5194/acpd-11-8173-2011, 2011.

17117

- Zhang, J. M., Wang, T., Ding, A. J., Zhou, X. H., Xue, L. K., Poon, C. N., Wu, W. S., Gao, J., Zuo, H. C., Chen, J. M., Zhang, X. C., and Fan, S. J.: Continuous measurement of peroxyacetyl nitrate (PAN) in suburban and remote areas of western China, Atmos. Environ., 43, 228-237. 2009.
- 5 Zhang, Y. N., Xiang, Y. R., Chan, L. Y., Sang, X. F., Wang, R., and Fu, H. X.: Procuring the regional urbanization and industrialization effect on ozone pollution in Pearl River Delta of Guangdong, China, Atmos. Environ., 45, 4898-4906, 2011.

Table 1. PAN levels measured in this study and observed in other locations.

Location Period PAN ^a PAN ^b Altitude ^c Latitude, Longitude Urban Beijing, China Jan–Mar 2010 3.51 0.70 58 39.95 [°] N, 116.32 [°] E	Ref. ^d
Beijing, China Jan–Mar 2010 3.51 0.70 58 39.95° N, 116.32° E	
	1
Beijing, China Aug 2007 14.0 39.99° N, 116.31° E	2
Seoul Korea, Korea 2011 5.03 0.57 25 37.32° N, 126.50° E	3
Korea University, Korea May–Jun 2005 10.4 0.80 46 37.32° N, 127.05° E	4
Los Angeles, US May–Jun 2010 0.9	5
Riverside, US Aug–Dec 1967 58.0	6
Ichihara, Japan 1985–1994 0.38 35.52° N, 140.08° E	7
Roman, Italy Apr 2007 30.3 37 41.54° N, 12.30° E	8
Porto Alegre, Brazil May 1996–Mar 1997 6.67 0.4 10 30.3° S, 51.23° W	9
Berlin, Germany Aug 1998 2.50 52.65° N, 13.30° E	10
Mexico City, Mexico Apr-May 2003 8.0 19.36° N, 99.07° W	11
Athens, Greece Jul–Aug 2000 6.60	12
Taipei, Taiwan Jul 1992–Apr 1993 27.0 26 25.05° N, 121.54° E	13
Suburban	
Guangzhou, China Jan–Dec 2012 12.5 0.84 141 23.07° N, 113.43° E	14
Lanzhou, China Jun–Jul 2006 9.13 0.76 1631 36.13° N, 103.69° E	15
Huston, US Aug–Sep 2000 6.50 0.48 26.67° N, 95.06° W	16
Frjoles Mesa, US Oct 1987–Jan 1989 1.91 0.23 1950 35.88° N, 106.32° W	17
Mountain top	
Mt. Waliguan, China Jun–Jul 2006 1.40 0.44 3816 36.19° N, 86.70° E	15
Jungfraujoch, Japan Feb-Mar 2003 1.29 0.14 45.55° N, 7.98° W	18
Arctic	
Ekstrokm ice shelf Feb 1999 0.05 0.01 32	19
Brunt ice shelf Jul 2004–Jan 2005 0.05 0.009 32 75.6° S, 26.6° W	20
Marine Boundary Layer	
Atlantic Ocean May–Jun 1998 1.09 0.01 32	21
Baengyeong, Korea Aug 2010–Apr 2011 2.47 0.38 150 37.95° N, 124.51° E	22
Coastal	
Charleston, US Jul-Aug 2002 2.79 0.36 71.00° N, 42.5° W	23
Nopigia, Greece May–Jun 1999 1.9 35.53° N, 23.78° E	10
Island	
Rishiri Island, Japan Jun 1999 0.15 35 45.07° N, 141.12° E	24
Rishiri Island, Japan Jul 1999 0.09 35 45.07° N, 141.12° E	24
Rishiri Island, Japan Aug 1999 0.036 35 45.07° N, 141.12° E	24

^a Maxium value, ppbv.
 ^b Mean value, ppbv.
 ^c m a.s.l.
 ^c Reference: 1. Zhang et al. (2014); 2. Liu et al. (2010); 3. Lee et al., (2013); 4. Lee et al. (2008); 5. Pollack et al. (2013); 6. Taylor et al. (1969); 7. Watanabe et al. (1998); 8. Movassaghi et al. (2012); 9. Grosjean et al. (2007); 10. Rappengluck et al. (2003); 11. Marley et al. (2007); 12. Giavas et al. (2001); 13. Sun and Huang (1995); 14. this work; 15. Zhang et al. (2009); 16. Roberts et al. (2001); 17. Gaffney et al. (1993); 18. Whalley et al. (2007); 19. Jacobi et al. (1999); 20. Milis et al. (2009); 12. Jacobi and Schrems (1999); 22. Lee et al. (2012); 23. Roberts et al. (2007); 24. Tanimoto et al. (2002).

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Table 2. Comparison of PA concentrations from different studies.

Location	Average PA levels (pptv)	Period	Ref.
Guangzhou, China	0.072	May and Oct 2012	This study
Pasco, WA, US	< 0.003	Aug 1997	Gaffney et al. (1999)
Atlanta, US	0.03	Jul–Aug 1992	Aneja et al. (1999)
Beijing, China	0.0028	Jan–Mar 2010	Zhang et al. (2014)

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	NMHC Species	Formation of th Acetaldehyde	nree key PA Acetone	N precursors MGLYOX	Annual Average Concentration ^a	SD⁵
Alkane	Ethane	Yes	-	_	2.950	1.805
	Propane	Yes	Yes	_	3.616	2.102
	Isobutane	Yes	Yes	_	2.238	1.700
	Isopentane	Yes	Yes	_	1.734	1.438
	n-Pentane	Yes	Yes	_	1.267	1.106
	n-Butane	Yes	Yes	-	2.590	1.984
	n-Undecane	Yes	Yes	_	0.122	0.213
	n-Nonane	Yes	Yes	_	0.602	0.626
	n-Heptane	Yes	Yes	-	0.452	0.457
	n-Decane	Yes	Yes	_	0.267	0.272
	n-hexane	Yes	Yes	-	1.189	1.020
	n-Octane	Yes	Yes	-	0.307	0.300
	2,3-dimethylbutane	Yes	Yes	-	0.301	0.264
	2,2-dimethylbutane	-	-	-	0.452	0.290
	2-methylhexane	Yes	Yes	-	0.500	0.701
	3-methylhexane	-	-	-	0.563	0.484
	Cyclopentane	-	-	-	0.403	0.329
	Cyclohexane	-	-	-	2.534	1.210
	2-methylpentane	-	-	-	0.834	0.696
	3-methylpentane	_	-	_	0.830	0.676
	2-methylheptane	_	-	_	0.279	0.302
	3-methylheptane	-	-	-	0.215	0.381
	2,3-dimethylpentane	_	-	_	0.432	0.348
	2,4-dimethylpentane	_	-	_	0.368	0.288
	Methylcyclohexane	-	-	-	0.339	0.344
	Methylcyclopentane	_	-	_	0.640	0.588
	2,3,4-trimethylpentane	_	-	_	0.299	0.305
	2,2,4-trimethylpentane	-	_	_	0.224	0.279

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Table 3. Measured concentrations of NMHCs and their ability to form PAN precursors.

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Table 3. Continued.

	NMHC Species	Formation of th Acetaldehyde	nree key PA Acetone	N precursors MGLYOX	Annual Average Concentration ^a	SD⁵
Alkene	Ethylene	_	_	_	3.005	1.978
	Propylene	Yes	-	Yes	1.159	0.921
	1-Butene	Yes	_	-	0.504	0.372
	trans-2-Butene	Yes	-	-	0.429	0.379
	cis-2-Butene	Yes	-	-	0.375	0.342
	1-Pentene	Yes	-	-	0.467	0.302
	Isoprene	Yes	-	-	1.661	1.283
	trans-2-pentene	Yes	-	-	0.306	0.156
	cis-2-pentene	Yes	-	-	0.555	0.217
	2-Methyl-1-Pentene	-	-	-	0.453	0.359
Aromatics	Benzene	_	_	_	0.998	0.458
	Toluene	-	_	Yes	4.437	3.444
	Ethylbenzene	-	_	-	1.247	1.090
	m&p-Xylenes	-	_	Yes	1.874	1.735
	Styrene	-	-	-	0.424	0.381
	o-Xylene	-	-	Yes	0.699	0.656
	Isopropylbenzene	-	-	-	0.106	0.213
	n-Propylbenzene	-	-	-	0.195	0.212
	m-Ethyltoluene	-	-	-	0.266	0.243
	p-Ethyltoluene	-	-	-	0.303	0.308
	1,3,5-Trimethylbenzene	-	-	-	0.208	0.301
	o-Ethyltoluene	-	-	-	0.186	0.213
	1,2,4-trimethylbenzene	-	-	-	0.192	0.208
	1,2,3-trimethylbenzene	-	-	-	0.181	0.215
	m-Diethylbenzene	-	-	-	0.111	0.253
	p-Diethylbenzene	-	-	-	0.129	0.153
Others	Acetylene	_	_	_		

^a Units are in ppbv.

^b SD: standard deviation.

Table 4. Contributions of NMHCs to PAN production*.

	NMHCs species	PAN contribution	Percentage contribution (%)
Alkane	Ethane	0.0008	<1
	Propane	0.0047	< 1
	Isopentane	0.0092	1.1
	Isobutane	0.0063	< 1
	2,3-Dimethylbutane	0.0024	< 1
	n-Pentane	0.0064	< 1
	n-Hexane	0.0088	1.0
	n-Heptane	0.0041	< 1
	n-Nonane	0.0086	1.0
	2-methylhexane	0.0032	< 1
	n-Octane	0.0010	< 1
	n-Decane	0.0023	< 1
	n-Undecane	0.0027	< 1
Alkane total		0.0605	< 7.2
Alkene	Propylene	0.0328	3.9
	1-Butene	0.0182	2.2
	trans-2-Butene	0.0316	3.8
	cis-2-Butene	0.0251	3.0
	1-Pentene	0.0183	2.2
	Isoprene	0.2467	29.4
	trans-2-Pentene	0.0258	3.1
	cis-2-Pentene	0.0459	5.5
Alkene total		0.4444	53.1
Aromatics	Toluene	0.0329	3.9
	m-&p-Xylenes	0.0456	5.4
	o-Xylene	0.0118	1.4
Aromatics total		0.0903	10.8
NMHCs total		0.60	~ 70

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* Units for all species are in ppbv.

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	Correlation coefficient	PAN	O ₃	NO	NO ₂	NO _x	NMHCs
Daytime							
Jan–Mar	PAN	1					
	O ₃	-0.162 ^a	1				
	NO	0.213 ^b	-0.314 ^b	1			
	NO ₂	0.262 ^b	0.339 ^b	0.291 ^b	1		
	NO_x^{a}	0.278 ^b	-0.108	0.916 ^b	0.650 ^b	1	
	NMHCs	0.188 ^a	-0.072	0.716 ^b	0.450 ^b	0.757 ^b	1
Apr–Jun	PAN	1					
	O ₃	0.212 ^b	1				
	NO	-0.064	–0.218 ^b	1			
	NO_2	0.042	-0.414 ^b	0.160 ^b	1		
	NO _x ^a	-0.027	-0.387 ^b	0.852 ^b	0.653 ^b	1	
	NMHCs	-0.030	-0.303 ^b	0.132 ^b	0.514 ^b	0.374 ^b	1
Jul–Sep	PAN	1					
	O ₃	0.317 ^b	1				
	NŐ	-0.283 ^b	-0.557 ^b	1			
	NO_2	-0.241 ^b	-0.340 ^b	0.452 ^b	1		
	NO ^{¯a}	-0.296 ^b	-0.484 ^b	0.753 ^b	0.928 ^b	1	
	NMHCs	-0.045	-0.141 ^b	0.061	-0.016	0.014	1
Oct-Dec	PAN	1					
	O ₃	0.402 ^b	1				
	NŎ	-0.238 ^b	-0.508 ^b	1			
	NO ₂	-0.160 ^b	-0.275 ^b	0.536 ^b	1		
	NO ^{[^]a}	-0.218 ^b	-0.421 ^b	0.824 ^b	0.920 ^b	1	
	NMHCs	-0.102 ^a	-0.104 ^a	0.136 ^b	0.114	0.140 ^a	1

Table 5. Results of correlation analysis between PAN and relevant pollutants measured at

 GPACS in daytime and nighttime during different seasons of 2012.

Table 5. Continued.

	Correlation coefficient	PAN	O ₃	NO	NO ₂	NO _x	NMHCs
Nighttime							
Jan–Mar	PAN O_3 NO NO_2 NO_x^a NMHCs	1 -0.099 ^b 0.326 ^b -0.054 ^b 0.261 ^b 0.299 ^b	1 -0.280 ^b 0.537 ^b 0.022 ^b -0.232 ^b	1 -0.120 ^b 0.858 ^b 0.795 ^b	1 0.407 ^b 0.010 ^b	1 0.737 ^b	1
Apr–Jun	PAN O_3 NO NO_2 NO_x^a NMHCs	1 0.232 ^b -0.146 ^b 0.174 ^b 0.039 0.004	1 -0.359 ^b -0.134 ^b -0.298 ^b -0.196 ^b	1 0.236 ^b 0.735 ^b 0.411 ^b	1 0.833 ^b 0.527 ^b	1 0.601	1
Jul–Sep	PAN O_3 NO NO_2 NO_x^a NMHCs	1 0.263 ^b -0.135 ^b 0.052 -0.048 ^a -0.017	1 -0.348 ^b -0.262 ^b -0.382 ^b 0.024	1 0.256 ^b 0.766 ^b -0.095 ^b	1 0.817 ^b -0.056	1 -0.094 ^b	1
Oct-Dec	PAN O_3 NO NO_2 NO_x^a NMHCs	1 0.089 ^a -0.129 ^a 0.030 -0.073 -0.101 ^a	1 -0.317 ^b -0.374 ^b -0.391 ^b -0.040	1 0.509 ^b 0.911 ^b 0.108	1 0.819 ^b 0.137 ^b	1 0.137 ^a	1

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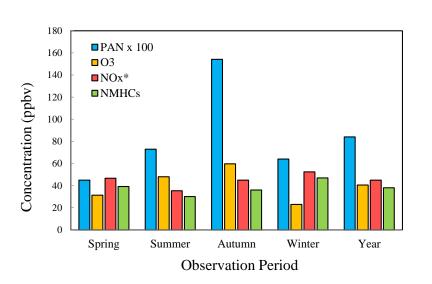
^a Correlation is significant at the 0.05 level.

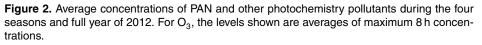
^b Correlation is significant at the 0.01 level.

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Figure 1. Location of Guangzhou Panyu Atmospheric Composition Station.







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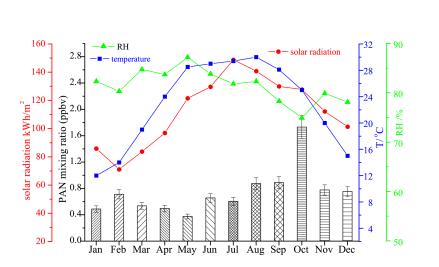
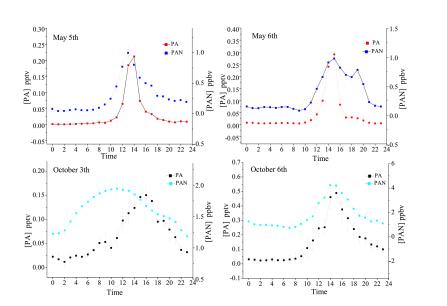


Figure 3. Monthly variations of PAN, temperature, solar radiation, and RH during the monitoring period.



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Figure 4. Estimated hourly concentrations of the PA $(CH_3C(O)O_2)$ radical at GPACS on 5 and 6 May, 3 and 6 October. Each hourly concentration is an average of six 10 min PA concentrations, which were calculated from 10 min measurements using Eq. (4). The vertical bars represent standard error. This is one example of several such periods throughout the measurement period.



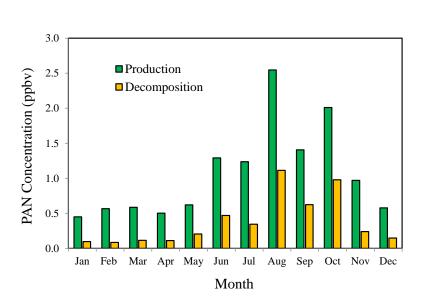
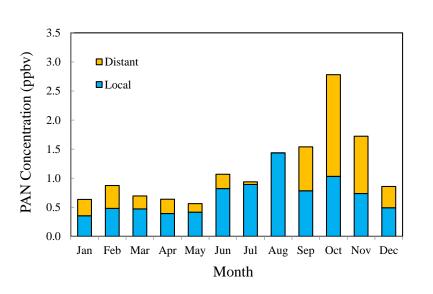
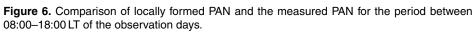


Figure 5. Calculated monthly average PAN formation and decomposition for the period between 08:00–18:00 LT of the observation days.



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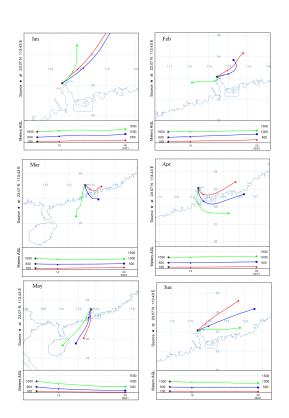
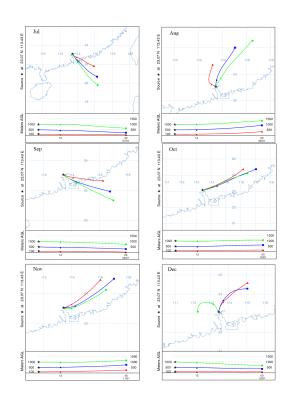


Figure 7.



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Figure 7. Back trajectories of air masses simulated using HYSPLIT.