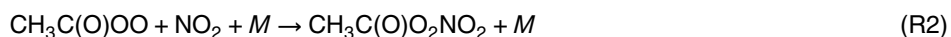


harmful to human health at a concentration as low as 5 ppbv (Taylor et al., 1969; WHO, 1987; Sun and Huang, 1995).

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).



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 impact the PA radical production (Altshuler, 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

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(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 O₃ formation (Crutzen, 1979; Ridley et al., 1990; Hudman et al., 2004).

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 O₃, 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 O₃ are formed from reactions of NO_x and VOCs following 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 O₃ concentration (e.g., Tsani-Bazaca et al., 1988; Glavas et al., 2001; Zhang et al., 2009), other studies have failed to show a correlation 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-

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 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, O₃, NO_x and non-methane hydrocarbons (NMHCs) as well as meteorological data. Using these data, we examined the variation of PAN concentration over an entire year and the relationship between PAN and other photochemical pollutants (O₃, 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.

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 elevation of 141 m a.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 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., 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 monitoring 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 × 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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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 study site (Fig. 2). The annual average concentrations of PAN and O₃ were 0.84 and 40.5 ppbv, respectively, while the annual average concentrations of NO₂, 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 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 summer 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

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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

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 continuous 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.



Because the concentrations of both PAN and NO₂ 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).

$$[\text{PA}] = \frac{k_3[\text{PAN}]}{k_2[\text{NO}_2]} \quad (2)$$

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

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

	NMHC Species	Formation of three key PAN precursors			Annual Average Concentration ^a	SD ^b
		Acetaldehyde	Acetone	MGLYOX		
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. Continued.

	NMHC Species	Formation of three key PAN precursors			Annual Average Concentration ^a	SD ^b
		Acetaldehyde	Acetone	MGLYOX		
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.

17122

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

* Units for all species are in ppbv.

17123

Table 5. Results of correlation analysis between PAN and relevant pollutants measured at GPACS in daytime and nighttime during different seasons of 2012.

	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				
	NO	-0.283 ^b	-0.557 ^b	1			
	NO ₂	-0.241 ^b	-0.340 ^b	0.452 ^b	1		
	NO _x ^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				
	NO	-0.238 ^b	-0.508 ^b	1			
	NO ₂	-0.160 ^b	-0.275 ^b	0.536 ^b	1		
	NO _x ^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

17124

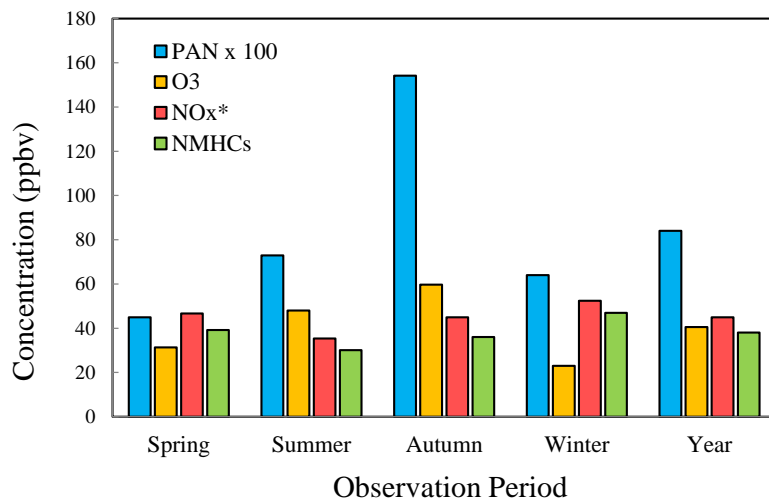


Figure 2. Average concentrations of PAN and other photochemistry pollutants during the four seasons and full year of 2012. For O₃, the levels shown are averages of maximum 8 h concentrations.

17127

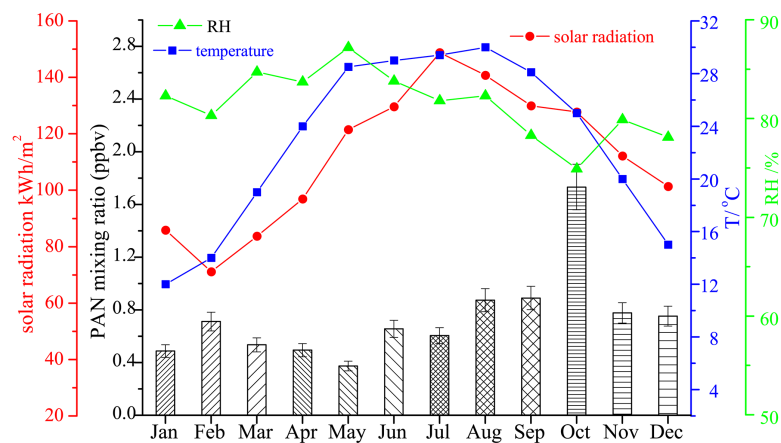


Figure 3. Monthly variations of PAN, temperature, solar radiation, and RH during the monitoring period.

17128

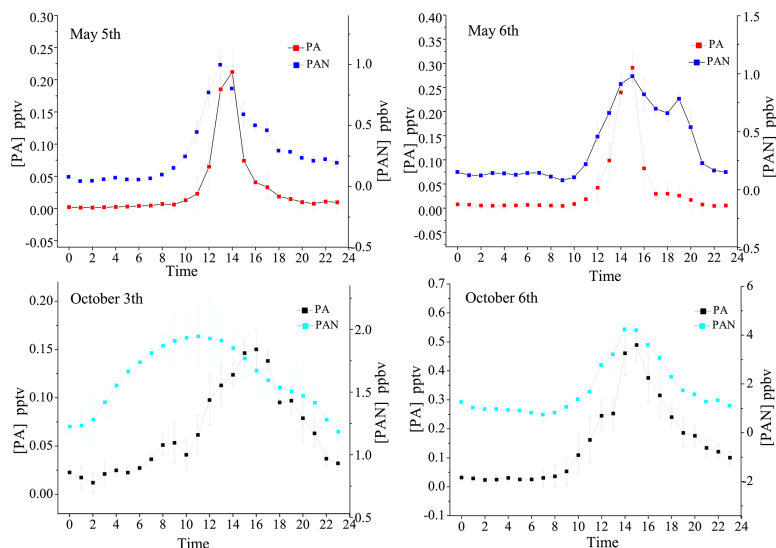


Figure 4. Estimated hourly concentrations of the PA ($\text{CH}_3\text{C}(\text{O})\text{O}_2$) radical at GPACS on 5 and 6 May, 3 and 6 October. Each hourly concentration is an average of six 10 min PA concentrations, which were calculated from 10 min measurements using Eq. (4). The vertical bars represent standard error. This is one example of several such periods throughout the measurement period.

17129

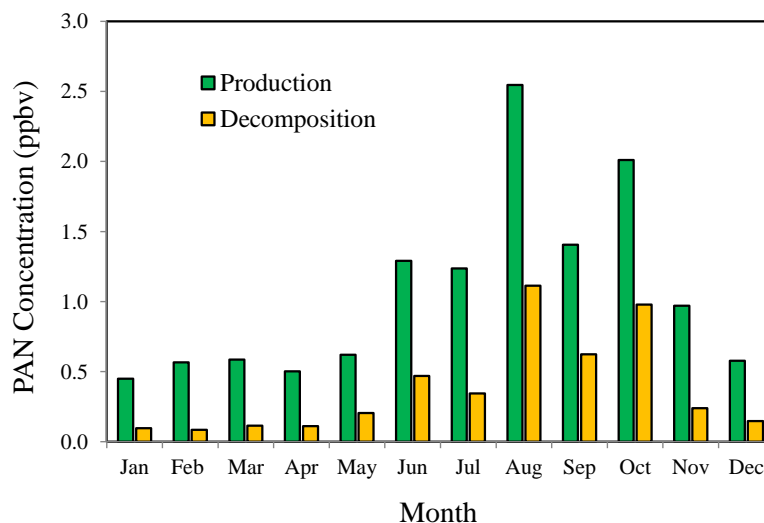


Figure 5. Calculated monthly average PAN formation and decomposition for the period between 08:00–18:00 LT of the observation days.

17130

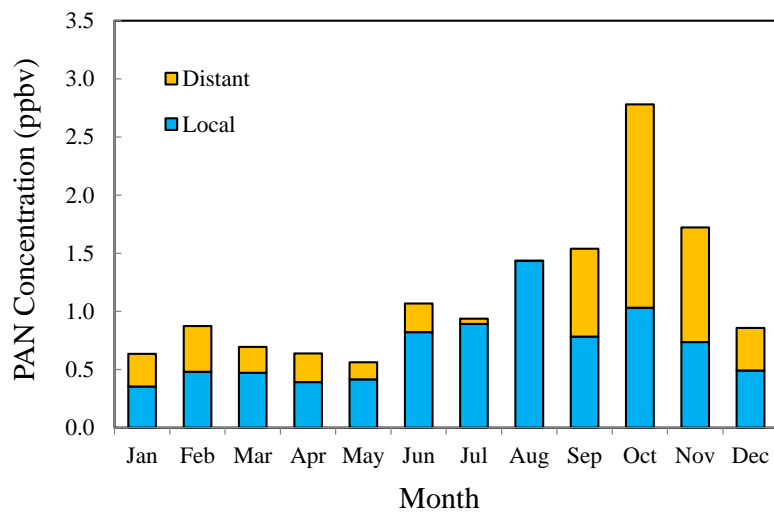


Figure 6. Comparison of locally formed PAN and the measured PAN for the period between 08:00–18:00 LT of the observation days.

17131

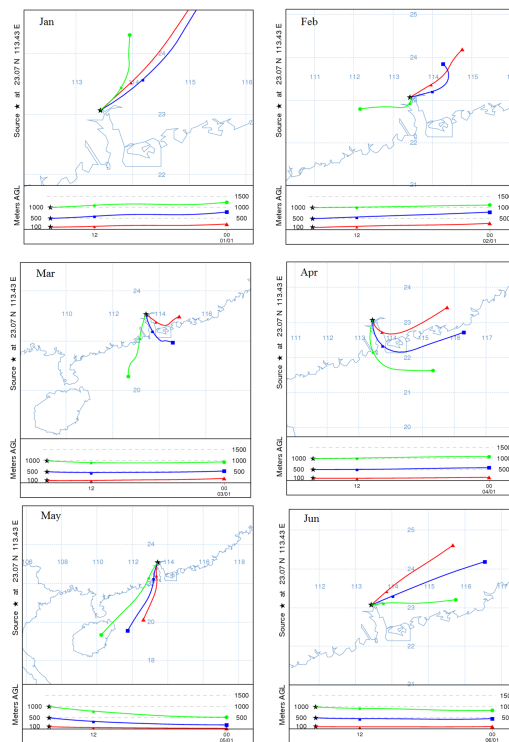


Figure 7.

17132

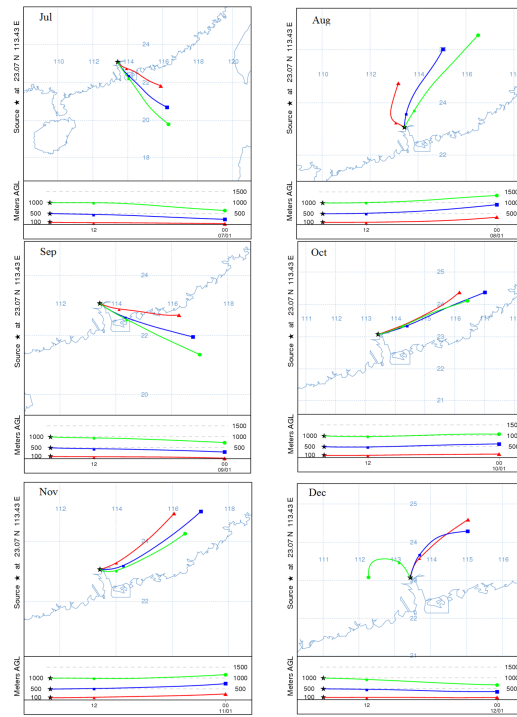


Figure 7. Back trajectories of air masses simulated using HYSPLIT.