Measurements of Peroxyacetyl Nitrate at a Background Site in the Pearl River Delta Region: Production Efficiency and Regional Transport

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ABSTRACT

Peroxyacetyl nitrate (PAN) is a trace constituent of the atmosphere but plays important roles in air pollution and atmospheric chemistry. To understand the chemical and transport processes of PAN in the Pearl River Delta (PRD) region, measurements of PAN, its precursors and related parameters were made at a regional background site in late summer and late autumn of 2011. Despite the fairly low ambient levels of PAN in general, several photochemical episodes with peak concentrations of PAN and ozone (O3) as high as 4.86 and 189 ppbv were observed when the region was under influence of a tropical cyclone. PAN showed a seasonal variation with higher levels in autumn than in summer. PAN production efficiency, defined as the amount of PAN formed per unit amount of nitrogen oxides (NOx) oxidized, was examined for the polluted PRD plumes, which indicated that PAN production accounted for on average approximately one third of the NOx formation. The photochemical production efficiency of PAN was much lower with respect to that of O3, suggesting that ~2.9 ppbv of PAN could be produced per formation of 100 ppbv of O3 in the PRD plumes. Varying air masses including maritime air, regional air masses from the PRD, and continental outflow from eastern China were identified, which showed different chemical signatures in terms of both pollution levels and NOx budget. The highest abundances of PAN were measured in the PRD air masses, compared to the lowest concentrations in the marine air. Overall, the present study provides some new insights into the photochemical production and regional transport of PAN in the PRD region, where such investigations were very scarce before.

Keywords: Peroxyacetyl nitrate; PAN production efficiency; Regional transport; Pearl River Delta.

INTRODUCTION

Peroxyacetyl nitrate (PAN) is a principal air pollutant in photochemical smog and a key player in atmospheric chemistry. At high concentrations, PAN poses a potential threat to the human health by causing eye irritation and inducing skin cancer, and also affects adversely vegetation and plant (Stephens, 1969). Due to its temperature-dependent lifetimes, PAN can be transported over long distances at low temperature conditions (e.g., in winter or in the free troposphere) and decompose to nitrogen dioxide (NO2) when entering warm environments (Singh and Salas, 1983).

This process re-distributes nitrogen oxides (NOx) over a large scale (regionally and even globally) and regulates ozone (O3) production in both source and remote regions (Penkett and Brice, 1986; Singh et al., 1986). In the troposphere, PAN is produced exclusively from chemical reactions involving NOx and volatile organic compounds (VOCs) in the presence of sunlight, and hence is a better photochemical indicator than O3 that can be influenced by downward transport of the stratospheric air (LaFranchi et al., 2009; Zhang et al., 2009a). Given its important roles in air pollution and atmospheric chemistry, PAN has drawn much attention since it was first discovered in the atmosphere of Los Angeles in 1950s (Grosjean, 2003).

Numerous studies have been conducted to characterize the PAN pollution and understand its formation mechanisms and transport behaviors in America, Europe and Japan (Singh and Hanst, 1981; Aneja et al., 1999; Gaffney et al., 1999; Grosjean et al., 2002; Rubio et al., 2004). In recent, several measurement studies have also been carried out in China, over which there is an increasing concern of air quality accompanying its fast economic development (e.g.,
in Lanzhou, Zhang et al., 2009a; Beijing, Liu et al., 2010; Zhang et al., 2011; Xue et al., 2014a). The Pearl River Delta region (PRD) including the adjacent Hong Kong is a hot spot of economic development and air pollution in southern China (Zhong et al., 2013). Previous studies have demonstrated the severity of the photochemical smog problem in this region (Zhang et al., 2007; Zhang et al., 2008; Xue et al., 2014b). Despite the large body of research on O3 processes (Ding et al., 2004; Zhang et al., 2007; Zhang et al., 2008; Zhang et al., 2012; Ling et al., 2014; Xue et al., 2014c), little has been known about the characteristics and processes of PAN in the PRD. To the best of our knowledge, there is only one piece of measurement study that was conducted downwind of Guangzhou city and the data was analyzed to understand the ozone formation (Wang et al., 2010a). More efforts are required for better understanding the PAN pollution and processes in this ‘smog’ region.

In the present study, field measurements of PAN, its precursors, and related parameters were conducted at a rural coastal site of Hong Kong (Hok Tsui) in summer and autumn of 2011. The site is an ideal regional background station of southern China that is capable of measuring varying air masses, including oceanic air, polluted plumes from the PRD region, and continental outflow from eastern China (Wang et al., 2009), and hence facilitates an investigation of PAN processes in a regional scale. The data were analyzed to understand the temporal variations, photochemical production efficiency, and regional transport of PAN (and related compounds) in southern China. The present study provides some new insights into the photochemical and transport characteristics of PAN in Hong Kong and the PRD region.

**EXPERIMENTAL**

The field measurements were carried out at the Hong Kong Polytechnic University's atmospheric research station at Hok Tsui (22.22°N, 114.25°E), which is located in the southeastern tip of Hong Kong Island with a 240° sea view from northeast to southwest (see Fig. 1). The station is established on a small cliff with an altitude of around 60 m above sea level. The air flow is mainly driven by the Asian Monsoons. In summer monsoon seasons, the prevailing wind is southerly, bringing fresh marine air to the station; while in winter monsoon seasons, the prevailing wind direction is northeasterly, so the air pollutants from the PRD region and East China can be carried to the site. Thus this site is capable of measuring varying air masses such as marine air, regional plumes from the PRD, and super-regional air masses from eastern China. It should be noted that the emissions from ships passing over the nearby ocean may also affect the site occasionally. The station has been used as a regional background site in many previous studies, which can be referred for detailed description of the site (Wang et al., 2001). The present study consisted of two separate campaigns, which took place from August 19th to September 16th 2011 and from November 09th to December 05th 2011, respectively.

PAN, O3, NO, NO2, NOy, CO, non-methane hydrocarbons (NMHCs) and meteorological parameters were continuously measured during the campaigns. PAN was measured by using a commercially available automatic instrument together with a calibration unit. The analyzing process is based on gas chromatographic (GC) separation coupled with electron capture detection, as illustrated by Schrimpf et al. (1995). The instrument was calibrated weekly using the stable flow of air containing pre-determined PAN concentrations produced by the calibration unit. PAN was synthesized by reactions of known concentrations of NO with excess acetone in the presence of ultra-pure air with a penray lamp. The produced PAN was then diluted to the desired concentration by mixing with the synthetic zero air. The sensitivity of analyzer can be determined from the slope of concentration versus signal, and was found to be stable throughout the campaigns. The linearity of analyzer was also evaluated by performing multi-point calibrations before and after the campaigns. This analyzer has been successfully utilized in our previous studies, from which detailed descriptions of instrument and measurement protocols can be found (Zhang et al., 2009a; Xue et al., 2014a).

O3 was measured using an ultraviolet photometric instrument (Thermo Environmental Instruments (TEI), Model 49C). CO was measured with a modified gas filter correlation, non-dispersive infrared analyzer (TEI, Model 48). NOy was measured by using a commercial chemiluminescence analyzer (Teledyne API, Model T200U) coupled with an outside placed molybdenum oxide (MoO) converter. NO and NO2 were measured by a chemiluminescence analyzer (TEI, Model...
coupled with a highly selective photolytic converter (Droplet Measurement Technologies, Model Blue Light Converter) (Xu et al., 2013). C2-C10 NMHCs were measured with a commercial instrument combining GC separation, flame ionization detection and photoionization detection (Syntech Spectras, Model GC955 Series 600/800 POCP). Total non-methane hydrocarbons were measured by a back-flush GC system (TEI, Model 55i). Temperature, relative humidity (RH), and wind speed and direction were monitored by a commercial probe (M. R. Young, Model 41382VC/VF) and a two-axis ultrasonic wind sensor (Gill Instruments, Model 1405-PK-021). The time frequencies of measurements were 10 minutes for PAN, 30 minutes for NMHCs, and 1 minute for other parameters. In addition, acetaldehyde was measured at a 24-hour frequency on selected days by collecting air samples in 2,4-DNPH-coated sorbent cartridge with subsequent high-pressure liquid chromatography detection (Xue et al., 2014a). Detailed descriptions of these measurements can be found in our previous studies (Wang et al., 2001; Wang et al., 2003a).

RESULTS AND DISCUSSION

Data Overview

Fig. 2 depicts the temporal variations in trace gases and meteorological parameters observed at Hok Tsui. The measurement period covered two seasons, i.e., late summer (19th August–16th September) and later autumn (9th November–5th December). A clear seasonal variation in the meteorological and pollution conditions is illustrated. In summer, diverse surface winds (both southerly and northerly) and higher temperature (and RH to a lesser extent) were recorded. The concentrations of PAN and other species were at a relatively low level during the majority of time, due to the southerly marine inflow and/or high temperatures (for PAN). A multi-day photochemical episode occurred during 25th–31st August 2011 when Hong Kong was under the influence of a distant tropical cyclone. Northerly winds brought polluted plumes from the PRD region, which coupled with the stagnant weather conditions contributed to the maximum pollution (i.e., 4.96 ppbv and 189 ppbv of 10-minute PAN and O3) observed during both campaigns. In comparison, strong northeasterly winds clearly dominated throughout the autumn phase, corresponding to the continental outflow to the measurement site. As a consequence, the overall pollution levels in autumn were higher than those in summer except for the typhoon-related episodes. Such a seasonal pattern is believed to be driven by the Asian Monsoons.

To make the results in a quantitative perspective, statistics of PAN and related species were calculated and summarized in Table 1. The average concentrations of PAN, NOx, CO and O3 were 0.48 (±0.69; standard deviation) ppbv, 10.3 (±9.8) ppbv, 191 (±141) ppbv and 33 (±25) ppbv in summer, and were 0.69 (±0.46) ppbv, 8.8 (±6.5) ppbv, 311 (±140) ppbv and 46 (±19) ppbv in autumn. Ten days were noticed with the peak 10-minute data of PAN exceeding 2 ppbv, and five days with the maximum PAN over 3 ppbv. The maximum values of PAN and O3 were recorded at 4.96 ppbv and 189 ppbv during the afternoon of 31st August 2011. Overall, the results indicated fairly low levels of pollution in general as well as severe pollution episodes under unfavorable conditions (e.g., typhoon) at this regional background site.

Statistics on selected VOC species that are major precursors of PAN are also provided in Table 1. The average mixing ratios (± SD) of propene, toluene, m/p-xylene, o-xylene and acetaldehyde were 0.45 (± 0.29), 0.95 (± 1.08), 0.48 (± 0.67), 0.27 (± 0.39) and 1.07 (± 1.07) ppbv in summer, and 0.22 (± 0.14), 1.11 (± 1.13), 0.21 (± 0.69), 0.11 (± 0.12) and 1.27 (± 0.42) ppbv in autumn. The fairly low levels are

Fig. 2. Time series of trace gases and meteorological parameters observed at Hok Tsui during August 19th–September 16th and November 9th–December 5th, 2011. The character “E” indicates the episodes with the peak PAN concentration exceeding 3 ppbv.
in consistence with the regional background nature of the study site. Air masses arriving at Hok Tsui either had been less influenced by fresh anthropogenic emissions or had undergone photochemical processing. An interesting result is that the aromatic precursors were generally more abundant than the alkene precursors, implying that the aromatics may play an important role in PAN formation in Hong Kong.

Fig. 3 presents the average diurnal variations of PAN, O\(_3\), CO, NO and NO\(_y\) observed at Hok Tsui. CO and NO showed the maximum concentrations in the morning, reflecting advection of fresh urban plumes to the study site. NO\(_y\) showed a coincident concentration peak in the morning reflecting advection of fresh urban plumes to the study site. O\(_3\) presented a typical diurnal pattern characteristic of rural atmosphere, with the mixing ratios increasing from early morning (07:00 local time (LT)) to late afternoon (15:00 LT). The average daily O\(_3\) increment was approximately 30 ppbv, indicating fair photochemical ozone production at this regional background station.

PAN exhibited a well-defined diurnal pattern, similar to that of O\(_3\), with relatively stable lower concentrations at night and a clear increase during the daytime. The daytime increment of PAN was about 0.52 ppbv on average. The highest concentrations occurred at 14:00–15:00 LT (~0.90 ppbv), when the solar radiation was the most intensive and thus the photochemistry was the most active. At its maximum, PAN accounted for approximately 10% of NO\(_y\) and 25% of NO\(_x\). After that, PAN began to decline due to the gradually weakened photochemistry and continuous thermal decomposition, and reached its minimum (~0.40 ppbv) till the night. Also shown in Fig. 3 are the individual diurnal profiles of PAN in both summer and fall. PAN showed comparable maximum concentrations in the afternoon but distinct levels at nighttime in both seasons. The nighttime levels (~0.15 ppbv) in summer were much lower than those observed in autumn (~0.47 ppbv), which should be due to the import of marine air masses as well as faster thermal decomposition at higher temperatures in summer. On the other hand, the daytime increment was much larger in summer (~0.74 ppbv) than in autumn (~0.35 ppbv), indicating stronger photochemical production of PAN in summer. Overall, inspection of the diurnal profiles reveals the important roles of photochemical production and transport in the variations of PAN (and other pollutants).

**Production Efficiency of O\(_3\) and PAN**

Although PAN and O\(_3\) are co-products of photochemistry involving NO\(_x\) and VOCs, they have different production efficiencies. This is because PAN is only formed from certain kinds of VOCs that are precursors of the acetyl radical (CH\(_3\)CO), while O\(_3\) can be produced from oxidation processes of all VOCs (Grosjean et al., 2002). Correlation between PAN and O\(_3\) can provide some useful information on their photochemical production efficiencies. An excellent positive correlation between the daily maximum values of PAN and O\(_3\) at Hok Tsui is shown in Fig. 4 (r\(^2\) = 0.82). The slope of linear regression is 0.028 ppbv/ppbv, which indicates that approximately 2.8 ppbv of PAN could be produced on average during the formation of 100 ppbv of O\(_3\) in the air masses reaching Hok Tsui. This value is comparable to those determined at Back Garden, a rural site in the PRD region (0.015–0.028 ppbv/ppbv, Wang et al., 2010a), Nashville (0.025 ppbv/ppbv, Roberts et al., 2002), and Mexico City (0.02 ppbv/ppbv, Marley et al., 2007), but much lower than those obtained in Lanzhou (0.091 ppbv/ppbv, Zhang et al., 2009a) and Beijing (0.07 ppbv/ppbv, Zhang et al., 2011). This relatively low production efficiency of PAN with respect to O\(_3\) implies that PAN precursors only made a small fraction of the total VOCs in the upwind regions. Indeed, the sum concentration of the observed PAN precursors (see Table 1) only accounted for about 20% of the total VOCs at Hok Tsui. Another factor leading to the lower production efficiency of PAN should be the high temperature in the PRD region that facilitates thermal decomposition of PAN.

We further assessed the production efficiencies of O\(_3\) and PAN during the photochemical episodes with the peak PAN value exceeding 3 ppbv (27th–31st August 2011; see Fig. 2). Backward trajectories suggested that the plumes sampled at Hok Tsui were mainly originated from the PRD under influence of a tropical cyclone (figures not shown), and hence the results should be representative of the PRD region. Fig. 5 presents the strong positive correlations between simultaneous data of PAN versus O\(_3\) on the individual episode days (r\(^2\) = 0.71–0.99). The slopes of ΔPAN/ΔO\(_3\) were in the range of 0.013–0.031 ppbv/ppbv, with a ‘mean’ value (i.e., slope of correlation for all data) of 0.029 ppbv/ppbv.

| Table 1. Statistical summary of 10-minute measurement data at Hok Tsui. |
|-----------------|-----------------|-----------------|-----------------|-----------------|
|                 | Late summer     |                 | Late autumn     |                 |
|                 | Average | SD     | Max    | Min    | Average | SD     | Max    | Min    |
| PAN             | 0.48    | 0.69   | 4.96   | -      | 0.69    | 0.46   | 2.80   | -      |
| NO\(_y\)        | 10.3    | 9.8    | 119    | 0.6    | 8.8     | 6.5    | 65.9   | 1.7    |
| CO              | 191     | 141    | 1109   | -      | 311     | 140    | 841    | 71     |
| O\(_3\)         | 33      | 25     | 189    | 2      | 46      | 19     | 113    | 2      |
| ethane          | 1.64    | 1.31   | 7.59   | 0.40   | 3.31    | 1.45   | 9.60   | 0.83   |
| propene         | 0.45    | 0.29   | 3.19   | 0.06   | 0.22    | 0.14   | 1.11   | 0.05   |
| toluene         | 0.95    | 1.08   | 7.03   | -      | 1.11    | 1.13   | 11.2   | 0.05   |
| o-xylene        | 0.27    | 0.39   | 3.97   | -      | 0.11    | 0.12   | 0.83   | -      |
| m/p-xylene      | 0.48    | 0.67   | 7.77   | -      | 0.21    | 0.29   | 2.08   | -      |
| CH\(_3\)CHO     | 1.07    | 1.07   | 2.60   | 0.19   | 1.27    | 0.42   | 2.01   | 0.69   |

The units are ppbv. SD is standard deviation; ‘-’ means that the data is below detection limit.
Fig. 3. Average diurnal variations of PAN, O₃, NO, NOₓ, PAN/NOₓ, and NOₓ/NOᵧ observed at Hok Tsui. The individual profiles in summer and fall are also shown for PAN.

Fig. 4. Scatterplot of the daily maximum PAN versus daily maximum O₃ observed at Hot Tsui. These values agreed well with that derived from analysis of daily maximums (Fig. 4). Comparison with other studies suggests that the production efficiency of PAN in the PRD region seemed to be relatively lower than those in Beijing and Lanzhou (Zhang et al., 2009a; Zhang et al., 2011).

Ozone production efficiency (OPE) is usually defined as the number of O₃ molecules produced per each NOₓ molecule oxidized, and is determined as the slope of a scatterplot of O₃ versus NOₓ (Trainer et al., 1993; Wang et al., 2010b). In the present study, OPE values of 9.0–13.3 were derived for the individual episode days based on correlation analyses of daytime measurements (08:00–17:00 LT) of O₃ and NOₓ (see Fig. 6(a)). These high values suggest that photochemical ozone production at Hok Tsui was in a NOₓ-limited regime, which is in line with the rural nature of the atmosphere.

In the present study, we adopt a similar approach to estimate the PAN production efficiency (PPE), which is defined as the amount of PAN formed per unit amount of NOₓ oxidized. Similarly, it is calculated as the slope of the scatterplot of PAN versus NOₓ, and can provide useful information on the fraction of PAN production to the total NOₓ oxidation. PPE (i.e., ΔPAN/ΔNOₓ) is a better proxy of the fraction of NOₓ produced in the form of PAN than the PAN/NOₓ ratio, which is generally influenced by the different lifetimes between PAN and other NOₓ species. Fig. 6(b) shows the scatterplots of daytime (08:00–17:00 LT) data of PAN and NOₓ during the photochemical episodes. The derived PPE values were in the range of 0.17–0.38 ppbv/ppbv, with a `mean` value (i.e., the slope of correlation for all data) of 0.32 ppbv/ppbv. This indicates that on average only 32% of NOₓ were converted to PAN while the rest was oxidized to other forms of NOₓ such as nitric acid, inorganic nitrate, and other organic nitrates. These results provide useful insights into the NOₓ oxidation and NOₓ budget in the PRD plumes.

Impact of Regional Transport

To evaluate the influence of regional transport on the observed PAN levels, we classified all the air masses into several major groups based on cluster analysis of backward
trajectories. Three-day backward trajectories were calculated with the HYSPLIT model every hour during the measurement campaigns, and were then identified to four different groups with a cluster analysis approach (Wang et al., 2009). The average trajectories representative of the four air mass types are shown in Fig. 7. The four types were referred to here as “East China”, “Marine”, “PRD”, and “Central China + PRD”, the name of which suggests the origins and regions over which the air masses had passed. Throughout the measurement period, the “East China” group occurred the most (36% in percentage), followed by “PRD” (24%), “Marine” (24%) and “Central China + PRD” (16%). The transport pattern derived from the present study in summer and autumn of 2011 was consistent with the climatological one determined for the years of 1994–2007 at the same site by Wang et al. (2009).

In addition, we also examined the CO/NO\textsubscript{y} ratios to confirm the identification of air mass origins from the trajectory analyses. According to Wang et al. (2003b), air masses originating from Hong Kong usually had a relatively lower CO/NO\textsubscript{y} ratio (i.e. 3.9–6 ppb/ppmv); the PRD regional air masses contained a much larger one (i.e., ~20 ppb/ppmv); and the ratio in the aged air masses from eastern China was even much higher (near to 40, Wang et al., 2004; Li et al., 2007). The difference in the CO/NO\textsubscript{y} ratio should be ascribed to the difference in energy consumption and air mass ages (note that CO has a longer lifetime than NO\textsubscript{y} thus the ratio increases with the air mass aging). In the present study, the average CO/NO\textsubscript{y} ratio of the “PRD” air masses was calculated as 18.2 ppb/ppmv, while those of the “East China” and “Central

![Fig. 5. Scatter plots of PAN versus O₃ during the selected photochemical episodes. The 10-min data at daytime (08:00–17:00, LT) are used.](image)

![Fig. 6. Scatter plots of (a) O₃ versus NOₓ and (b) PAN versus NOₓ during the selected photochemical episodes. The 10-min data at daytime (08:00–17:00, LT) are used.](image)
Fig. 7. Four major types of 3-day backward trajectory arriving at Hok Tsui during the observation periods. The percentage of each type is also given. The anthropogenic NOx emission data is obtained from Zhang et al. (2009b).

Table 2. Chemical characteristics of the four types of air masses arriving at Hok Tsui.

<table>
<thead>
<tr>
<th>Air mass type</th>
<th>PAN (ppb)</th>
<th>NOx (ppb)</th>
<th>NOy (ppb)</th>
<th>CO (ppb)</th>
<th>O3 (ppb)</th>
<th>TNMHC (ppm)</th>
<th>NOx/NOy</th>
<th>CO/NOy</th>
<th>PAN/NOz</th>
<th>Temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marine</td>
<td>0.15</td>
<td>5.4</td>
<td>7.5</td>
<td>128</td>
<td>32</td>
<td>0.011</td>
<td>0.73</td>
<td>17.1</td>
<td>0.07</td>
<td>28</td>
</tr>
<tr>
<td>PRD</td>
<td>0.86</td>
<td>16.4</td>
<td>19.5</td>
<td>355</td>
<td>50</td>
<td>0.046</td>
<td>0.84</td>
<td>18.2</td>
<td>0.31</td>
<td>26</td>
</tr>
<tr>
<td>East China</td>
<td>0.62</td>
<td>3.0</td>
<td>5.9</td>
<td>276</td>
<td>51</td>
<td>0.013</td>
<td>0.50</td>
<td>46.7</td>
<td>0.17</td>
<td>24</td>
</tr>
<tr>
<td>Central China + PRD</td>
<td>0.61</td>
<td>8.7</td>
<td>10.1</td>
<td>412</td>
<td>35</td>
<td>0.038</td>
<td>0.86</td>
<td>40.9</td>
<td>0.34</td>
<td>21</td>
</tr>
</tbody>
</table>

China + PRD” were 46.7 ppb/ppb and 40.9 ppb/ppb, respectively (see Table 2). These results agree well with the previous studies and hence double validate the classification of different air masses.

Table 2 summarizes the average concentrations of PAN, O3, CO, NOx, NOy, total NMHCs and ratios of NOx/NOy, CO/NOy and PAN/NOz for the four types of air masses. The “Marine” air masses showed the lowest levels of PAN (0.15 ppbv) and other species as well. Note that the NOx and NOy levels in the “Marine” group were relatively higher than those in the “East China” group. This should be due to the occasional impact of fresh ship emissions, which is supported by the high ratio of NOx/NOy (0.73). In comparison, the highest levels of PAN (0.87 ppbv) and other pollutants were found in the “PRD” air masses. This was within the expectation in light of the intense anthropogenic emissions in the PRD region as well as the relatively short transport time to the measurement site. The “East China” and “Central China + PRD” groups contained comparable abundances of PAN (0.62 and 0.61 ppbv), but showed different profiles for the other species. Specifically, the more aged “East China” air masses had higher levels of O3 but lower concentrations of O3 (also PAN) precursors (i.e., NOx, CO and NMHCs), while an opposite pattern was found for the “Central China + PRD” group that may be influenced by fresh emissions in the PRD.

Also illustrated from Table 2 are the varying PAN/NOz ratios reflecting different NOz composition in different air masses. On average, PAN accounted for 31% and 34% of the NOz in the air masses of “PRD” and “Central China + PRD”. These values were consistent with the PAN production efficiency determined for the photochemical episodes (see Fig. 6(b)). In comparison, the “East China” air mass group showed a relatively lower ratio of 0.17, implying the predominant role of inorganic nitrates in the NOz compounds. The lowest PAN/NOz ratio (0.07) was found in the “Marine” air masses, which are believed to contain large amount of sea salt that is conductive to the production of inorganic nitrates. Overall, the above analyses highlight the significant role of regional transport in the ambient abundances of PAN and related pollutants in Hong Kong. The chemical signatures determined in the present study can be used for future studies to infer the origins of different air masses. The concentration of PAN in the “Marine” air masses could serve as the regional background value of southern China.

CONCLUSIONS

Intensive measurements were performed at Hok Tsui in the summer and autumn of 2011 to understand the chemical
and transport processes of PAN in the PRD region. The ambient concentrations of PAN and PAN precursors were fairly low at this rural site, with relatively higher levels in autumn than in summer. Severe photochemical episodes were observed under unfavorable conditions (i.e., typhoon-influenced) with the PAN and O₃ mixing ratios up to 4.96 and 189 ppbv. Different air masses including oceanic air, regional plumes from the PRD, and continental outflow from eastern China, were sampled during the measurement period, which showed distinct chemical signatures. The highest levels of PAN and other pollutants were found in the PRD regional plumes, whilst the lowest levels were measured in the oceanic air.

The photochemical production efficiencies of PAN and O₃ as well as NOₓ budget were examined in the polluted plumes from the PRD. The ozone production efficiency was in the range of 9.0–13.3 ppbv/ppbv, indicating that the local O₃ production was in a NOₓ-limited regime. The average PAN production efficiency was 0.32 ppbv/ppbv, indicating that about one third of the NOₓ was produced in the form of PAN in the PRD air masses. According to correlation analyses between PAN and O₃, about 2.9 ppbv of PAN was produced on average when 100 ppbv of O₃ was formed. The production efficiency of PAN with respect to O₃ in the PRD region was much lower than those determined in Beijing and Lanzhou, China. This study can provide useful information on the photochemical production and regional transport of PAN in the PRD region.

ACKNOWLEDGEMENTS

The authors would like to thank Steven Poon and Much Yeung for their help in the field measurements, and thank the NOAA Air Resources Laboratory for providing the HYPLIT model and meteorological data. We thank the anonymous reviewer for the helpful suggestions which helped improving the original manuscript. This work was funded by the Environment and Conservation Fund (Project No. 7/2009), the Hong Kong Research Grants Council (PolyU 5015/12P), and the Hong Kong Polytechnic University (1-ZV9N).

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Xu et al., Aerosol and Air Quality Research, 15: 833–841, 2015

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Received for review, November 5, 2014
Revised, January 29, 2015
Accepted, January 31, 2015