Decoupling peroxyacetyl nitrate from ozone in Chinese outflows observed at Gosan Climate Observatory

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Abstract. We measured peroxyacetyl nitrate (PAN) and other reactive species such as O3, NO2, CO, and SO2 with aerosols including mass, organic carbon (OC), and elemental carbon (EC) in PM2.5 and PM1.0 at Gosan Climate Observatory in Korea (33.17° N, 126.10° E) during 19 October–6 November 2010. PAN was determined through fast gas chromatography with luminol chemiluminescence detection at 425 nm every 2 min. The PAN mixing ratios ranged from 0.1 (detection limit) to 2.4 ppbv with a mean of 0.6 ppbv. For all measurements, PAN was unusually better correlated with PM2.5 (Pearson correlation coefficient, γ = 0.79) than with O3 (γ = 0.67). In particular, the O3 level was highly elevated with SO2 at midnight, along with a typical midday peak when air was transported rapidly from the Beijing areas. The PAN enhancement was most noticeable during the occurrence of haze under stagnant conditions. In Chinese outflows slowly transported over the Yellow Sea, PAN gradually increased up to 2.4 ppbv at night, in excellent correlation with a concentration increase in PM2.5 OC and EC, PM2.5 mass, and PM1.0 K+. The high K+ concentration and OC/EC ratio indicated that the air mass was impacted by biomass combustion. This study highlights PAN decoupling with O3 in Chinese outflows and suggests PAN as a useful indicator for diagnosing continental outflows and assessing their perturbation of regional air quality in northeast Asia.

1 Introduction

At the surface, ozone is primarily photochemically produced, and the contribution from the stratosphere is generally small. Ozone is formed through reactions of various precursors such as CO, CH4, volatile organic compounds (VOCs), and NOx (e.g., Brasseur et al., 1999; Jacob, 2000; Nielsen et al., 1981). Likewise, peroxyacetyl nitrate (PAN) is a secondary product of urban air pollution and a significant oxidant in the atmosphere (e.g., Hansel and Wisthaler, 2000; LaFranchi et al., 2009; Lee et al., 2012; Liu et al., 2010; Roberts et al., 2007). PAN is solely produced by the photochemical reaction between the peroxyacetyl radical and nitrogen dioxide, and the peroxyacetyl radical is derived from the OH oxidation or photolysis of VOCs such as acetaldehyde, methylglyoxal, and acetone (e.g., Fischer et al., 2014; LaFranchi et al., 2009; Lee et al., 2012; Liu et al., 2010; Roberts et al., 2007). PAN is a major PAN sink in the troposphere (Beine et al., 1997; Jacob, 2000; Kenley and Hendry, 1982; Talukdar et al., 1995), the lifetime of PAN depends on temperature. For example, the PAN lifetime is ∼5 years at −26°C and 1 h at 20°C (Fischer et al., 2010; Zhang et al., 2011). At high altitudes above ∼7 km, photolysis becomes the most important loss process for PAN (Talukdar et al., 1995). Because of low solubility, PAN is not prone to atmospheric removal, thereby being more efficiently transported to the free troposphere (e.g., Zhu et al., 2017). Thus, PAN can be an indicator of NOy concentration in the free troposphere and a guide for
the long-range transport of NO\textsubscript{x} in remote regions (Jacob, 1999).

In the past decades, PAN has been measured not only in urban areas (Aneja et al., 1999; Gaffney et al., 1999; Grosjean et al., 2002; Lee et al., 2008; Tanimoto et al., 1999; Zhang et al., 2014) but also in background regions (Fischer et al., 2011; Kanaya et al., 2007; Lee et al., 2012; Tanimoto et al., 2002), on board aircraft (Tereszchuk et al., 2013), and ships (Roberts et al., 2007). PAN concentrations were in the range of a few ppbv in urban areas close to VOCs and NO\textsubscript{x} sources (Lee et al., 2008; Zhang et al., 2011). In the most remote regions, PAN concentrations were generally in the range of a few pptv (Gallagher et al., 1990; Mills et al., 2007; Muller and Rudolph, 1992; Staudt et al., 2003).

Although NO\textsubscript{x} concentration has recently declined in China (Gu et al., 2013; F. Liu et al., 2016; Krotkov et al., 2016), NO\textsubscript{x} and VOCs have gradually increased in East Asia, particularly China during the last couple of decades (Aki-moto, 2003; Liu et al., 2010; Ohara et al., 2007; Zhao et al., 2013). This led to an increase in the concentrations of photochemical byproducts such as PAN and O\textsubscript{3} not only in East Asia (Liu et al., 2010; Wang et al., 2010; Zhang et al., 2009, 2011, 2014) but also in North America (Fischer et al., 2010, 2011; Jaffe et al., 2007; Zhang et al., 2008). These results were also demonstrated by the GEOS-Chem model (Zhang et al., 2008). In addition to urban plumes, PAN was reported to be enhanced by biomass combustion (Alvarado et al., 2010; Coheur et al., 2007; Zhu et al., 2015, 2017), such as open burning and the use of biofuel, which often takes place in China after crop harvesting (Cao et al., 2006; Duan et al., 2004). Recent satellite studies have also observed the increased PAN in plumes associated with anthropogenic emissions in eastern China and boreal fires in Siberia (Zhu et al., 2015, 2017). In this context, PAN is a useful tracer for estimating the impact of Chinese outflows on regional air quality in the northern Pacific region.

Gosan Climate Observatory (GCO) is an ideal place to monitor Asian outflows and their transformation and to estimate their impact on air quality over the northern Pacific region (Lee et al., 2007; Lim et al., 2012). In the present study, PAN was first measured continuously at GCO to characterize its variation and source in relation to O\textsubscript{3} and to understand the influence of Chinese outflows on the regional air quality.

2 Experiments

PAN measurements were conducted at GCO (33.17° N, 126.10° E) on Jeju Island from 19 October to 6 November 2010. GCO is located on a cliff at the western edge of Jeju Island. PAN was determined through fast gas chromatography (GC) with luminol chemiluminescence detection, which is described in detail elsewhere (Gaffney et al., 1998; Lee et al., 2008; Marley et al., 2004). Here, we briefly describe the measurement method.

Ambient air was pumped through a 1.6 m PFA tubing (1/4 in. outer diameter) from the roof of the two-story container into a six-port injection valve (Cheminer C22, Valco Instruments (Houston, TX, USA)) at 100 mL min\textsuperscript{-1} controlled by a mass flow controller (Lee et al., 2012, 2008). The residence time of the inlet was less than 2 s. PAN and NO\textsubscript{2} (and peroxypropyl nitrate (PPN) if present) were separated along a 10 m capillary GC column (DB-1, J&W Scientific, Folsom, CA, USA), whose end was connected to a luminol cell where the column effluent reacted with luminol, giving off luminescent light (Lee et al., 2008, 2012). The concentrations of PAN and other species were determined from the chemiluminescence signals detected by a gated photon counter (HC135-01, Hamamatsu, Bridgewater, NJ, USA) at 425 nm, which was set to 800 V and operated at room temperature (Gaffney et al., 1998; Lee et al., 2012, 2008).

PAN was calibrated against standards synthesized by the nitration of peracetic acid in n-tridecane (Gaffney et al., 1984; Gregory, 1990; Lee et al., 2008). A few microliter aliquots of standard solution were injected through an injection valve and then mixed with zero air (99.999 %) in a 5 L Tedlar bag. After being left for a few minutes for equilibrium, it was injected into the GC–luminol instrument and the NO\textsubscript{x} chemiluminescence instrument with a molybdenum converter (42C, Thermo Electron Corporation, Franklin, MA, USA). The calibration was completed within 5 min to prevent thermal decomposition of the PAN (Kourtidis et al., 1993; Lee et al., 2008). These calibration procedures were carried out on the assumption that the PAN was completely converted to NO in the molybdenum converter. The detection limit of PAN defined by 3σ of the lowest standard was no greater than 100 pptv (Lee et al., 2008). The overall measurement uncertainty and precision were estimated to be 16 and 5 %, respectively (Lee et al., 2012). The NO\textsubscript{x} instrument was calibrated with NO standard gas.

Gaseous species including O\textsubscript{3}, NO, NO\textsubscript{2}, CO, and SO\textsubscript{2} were measured by UV absorption, chemiluminescence with a molybdenum converter, non-dispersive infrared, and the pulse UV fluorescence method (NIER, 2016a). The measurements were made in compliance with guidelines for the installation and operation of an air pollution monitoring network (NIER, 2016b). Calibration was conducted before and after the experiment, following the regular checkup procedure. The detection limits of O\textsubscript{3}, NO\textsubscript{x}, CO, and SO\textsubscript{2} are 2, 0.1, 50, 0.1 ppb, respectively (NIER, 2016b). It should be noted that the NO\textsubscript{2} concentration reported in the present study is actually the sum of NO\textsubscript{2} and NO\textsubscript{x} species due to a well-known positive artifact of the molybdenum convertor. PAN is one of the major NO\textsubscript{x} species, and the ratio of PAN to NO\textsubscript{2} was 12 ± 7 % for all measurements.

Aerosol species, including PM\textsubscript{2.5} mass and PM\textsubscript{2.5} organic carbon (OC) and elemental carbon (EC) were measured and recorded along with meteorological parameters (relative humidity, temperature, and wind direction and speed). Water-soluble ions of PM\textsubscript{1.0} were collected by a particle-into-liquid
Figure 1. Temporal variations (against local time) of measured species (PAN, PM$_{2.5}$, O$_3$, NO$_2$, NO, SO$_2$, and CO) and meteorological parameters (relative humidity, temperature, and wind speed) in fall 2010. Episodes 1–4, described in the main text, are shaded in blue and yellow.

sampler (PILS) and analyzed by ion chromatography. The detailed results of the aerosol measurements can be found in Shang et al. (2017).

For the air parcel at 850 m a.s.l., the 3-day backward trajectories were calculated every hour using the NOAA Air Resources Laboratory (ARL) Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model (version 4) (Draxler and Rolph, 2012; Rolph, 2012, http://www.arl.noaa.gov/ready/hysplit4.html). In addition, O$_3$ and PAN concentrations were calculated using a global chemistry model, the Community Atmosphere Model with Chemistry (CAM-chem), a component of the Community Earth System Model (CESM) (Lamarque et al., 2012; Tilmes et al., 2015). The CAM-chem results shown here follow the configuration used for the HTAP2 (Hemispheric Transport of Air Pollution, Phase 2) intercomparison (e.g., Stjern et al., 2016). CAM-chem is nudged to observed meteorology (GEOS-5) to reproduce the actual period of the observations (October 2010). The emissions used in the model are the HTAP2 inventory (Janssens-Maenhout et al., 2015), which include the MIX Asian emissions inventory. Biomass burning emissions are from the Global Fire Emissions Database (GFED3) (Randerson et al., 2013).

3 Results

In the present experiments, PAN concentrations range from 0.1 to 2.4 ppbv, with an average of 0.6 ppbv. This mean value is lower than those observed in other Asian megacities: Beijing (1.41 ppb in the summer), the Pearl River Delta region (1.32 ppb in the summer), and Seoul (0.8 ppb in the early summer); it is similar to those of suburban areas in China, e.g., Lanzhou (0.76 ppb in the summer), and higher than those of urban and rural sites in Japan (e.g., Tokyo (up to 0.6 ppb in the fall), Rishiri Island (~0.5 ppb in spring)), the western coast of the US (e.g., Sacramento (0.45 ppb in the spring), and over the remote North Pacific (total PAN < 0.3 ppb in spring) (Bertram et al., 2013; Fischer et al., 2011; LaFranchi et al., 2009; Lee et al., 2008; Roberts et al., 2004; Tanimoto et al., 1999, 2002; Wang et al., 2010; Zhang et al., 2009, 2011). Because the PAN lifetime is greatly dependent on temperature, its concentration decreases with increasing distance from the source regions. The PAN concentrations calculated in this study thus lie in between the levels for the East Asian megacities and the northern Pacific. The distributions of all measured species, including PAN and O$_3$, are presented in Fig. 1. In particular, there are several periods characterized by high concentrations of PAN, O$_3$, and...
PM\textsubscript{2.5}. In terms of PAN, four periods are particularly interesting (Fig. 1). High O\textsubscript{3} concentrations were observed during 31 October–2 November (episode 1) but did not coincide with high PAN concentrations. During 28–29 October (episode 2), NO\textsubscript{2} was noticeably increased. In comparison, PAN and O\textsubscript{3} concentrations were both high during 20–21 October (episode 3) and 4–5 November (episode 4). Episodes 3 and 4 are characterized by haze, while episodes 1 and 2 are characterized by urban influence in the Korean and Beijing outflows, respectively. Haze is reported by the Korea Meteorological Administration (KMA) as a meteorological phenomenon when visibility is 1–10 km and relative humidity is less than 75%.

In the present study, PAN correlates reasonably well with O\textsubscript{3} ($\gamma = 0.67$) and even better with PM\textsubscript{2.5} ($\gamma = 0.79$). In general, O\textsubscript{3} and PAN exhibit typical diurnal variation with a maximum recorded in the afternoon, which results in a good correlation between the two (Brasseur et al., 1999; Gaffney et al., 1999; Ridley et al., 1990; Schrimpf et al., 1995; Wang et al., 2010). In this study, however, the O\textsubscript{3} peak was often found in the early morning and late afternoon for several days (Fig. 1). Observing the diurnal variations in the entire PAN concentration measurement set (Fig. 2), the maximum was clearly recorded in the morning with the highest outliers, which is rather similar to that of PM\textsubscript{2.5}. The diurnal pattern of NO\textsubscript{2} shows little variation, even though its concentrations were increased in the morning along with PAN. This first measurement of PAN at GCO reveals that PAN is not always coupled with O\textsubscript{3}, which was not typically observed at remote sites in previous studies (e.g., Fischer et al., 2010; Lee et al., 2012).

4 Discussion

4.1 Decoupling of PAN from O\textsubscript{3}

To examine the detailed mechanism of the decoupling of PAN from O\textsubscript{3}, the daily maximum concentrations of PAN and O\textsubscript{3} were further explored. The recorded daily PAN maxima were generally in good correlation with O\textsubscript{3}, although the relationship did not seem to hold at high concentrations of PAN and O\textsubscript{3} (Fig. 3). The daily maxima were then categorized into four groups according to the time when each O\textsubscript{3} and PAN maximum was recorded: “O\textsubscript{3} day–PAN day”, “O\textsubscript{3} day–PAN night”, “O\textsubscript{3} night–PAN day”, and “O\textsubscript{3} night–PAN night”. The day interval started from 08:00 and ended at 18:00 (local time), based on the times of sunrise and sunset during the experiment period. While the high PAN concentrations were associated with the “O\textsubscript{3} day–PAN day” group (cross symbols in Fig. 3), the enhanced O\textsubscript{3} concentration was recorded in the “O\textsubscript{3} night–PAN night” group (star symbols in Fig. 3). The “O\textsubscript{3} night–PAN night” group unexpectedly held more data points than the “O\textsubscript{3} day–PAN day” group,
Table 1. Chemical and meteorological characteristics of the four episodes.

<table>
<thead>
<tr>
<th>Episode 1</th>
<th>Episode 2</th>
<th>Episode 3</th>
<th>Episode 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Period</td>
<td>31 October–2 November</td>
<td>28–29 October</td>
<td>20–21 October</td>
</tr>
<tr>
<td>Type</td>
<td>Transport dominant</td>
<td>Transport dominant</td>
<td>Chemical transformation</td>
</tr>
<tr>
<td>Event</td>
<td>O₃ export</td>
<td>O₃ export</td>
<td>Haze</td>
</tr>
<tr>
<td>O₃ (ppbv)</td>
<td>60.2 (80.6)</td>
<td>45.6 (62.8)</td>
<td>59.7 (78.9)</td>
</tr>
<tr>
<td>PAN (ppbv)</td>
<td>0.5 (0.9)</td>
<td>0.5 (0.8)</td>
<td>1.2 (2.0)</td>
</tr>
<tr>
<td>PM₂.₅ (µg m⁻³)</td>
<td>34 (62)</td>
<td>23 (36)</td>
<td>50 (76)</td>
</tr>
<tr>
<td>SO₂ (ppbv)</td>
<td>4.3 (12.9)</td>
<td>2.0 (4.4)</td>
<td>2.6 (5.4)</td>
</tr>
<tr>
<td>NO₂ (ppbv)</td>
<td>3.7 (7.3)</td>
<td>6.2 (12.1)</td>
<td>6.2 (12.7)</td>
</tr>
<tr>
<td>Wind Speed (m s⁻¹)</td>
<td>13.5 (16.0)</td>
<td>9.5 (16.1)</td>
<td>6.6 (10.2)</td>
</tr>
</tbody>
</table>

* Measurements are given for the average with the maximum in parentheses.

even though the “O₃ night–PAN night” group concentrations were lower (Fig. 3). In addition, several days were classified as belonging to the “O₃ night–PAN day” (marked by diamond) and “O₃ day–PAN night” groups, but they showed less frequency and lower concentrations. These results indicate that the decoupling of PAN from O₃ was primarily due to the elevated concentrations of O₃ and PAN at night. While PAN reached the maximum during the day on 20 October and 5 November, their concentrations were increased from the previous day through the night. The four high PAN and O₃ episodes identified in this study fall under the category of “O₃ night–PAN night” or “O₃ day–PAN day”. These two cases will be further examined to identify the chemical and physical processes responsible for PAN being decoupled from O₃, instead of being coupled with PM₂.₅. The overall characteristics of the four episodes are summarized in Table 1.

4.2 Export of O₃ from Asian continents (episodes 1 and 2)

High O₃ concentrations were encountered around midnight on three consecutive days from 31 October to 2 November (episode 1), during which SO₂ reached its maximum concentration (Fig. 1). The backward trajectories of air masses revealed that air passed through the Beijing area during this period (Fig. 4). The strong wind (13.5 m s⁻¹ on average) implies that it would take about a day for air mass leaving Beijing area to arrive at GCO. The recorded O₃ maximum (80.6 ppbv) was concurrent with the PAN maximum (0.9 ppbv) around midnight on 1 November (Fig. 1). All these results indicate that the air was heavily influenced by outflow from the Beijing area, as previously hypothesized (Lim et al., 2012), and that the nighttime enhancement of O₃ and PAN with SO₂ resulted from the fast transport of urban plumes from China.

In previous studies, the nighttime enhancement of O₃ was observed at GCO (e.g., Lee et al., 2007) in association with pollutant-laden air coming from Beijing. Similarly, Banta et al. (1998) pointed out that the evening O₃ maximum was due to long-range transport of O₃ from nearby urban areas. Wang et al. (2011) reported that the O₃ lifetime was about two days in east China during the summer, which is sufficient for O₃ to travel to GCO but not for PAN due to its short lifetime. Therefore, the nighttime maximum of O₃ can be attributed to the export of O₃ from megacities in China, causing PAN to be decoupled from O₃. Because the overall correlation between O₃ and PAN was the best with the highest ΔO₃/ΔPAN among all cases discussed in this study (Fig. 5a), episode 1 likely represents an event of rapid transport from the Beijing area.

Another night maximum of O₃ was recorded on 29 October. Note that NO₂ was highly elevated with the lowest SO₂ concentrations during 28–29 October (episode 2) (Fig. 1). In
Figure 4. The three-day NOAA HYSPLIT backward trajectories of air masses for every 1 h observed at GCO during episode 1 (31 October–2 November), episode 2 (28–29 October), episode 3 (20–21 October), and episode 4 (4–5 November). They are colored according to the level of (a) PAN, (b) \( \text{O}_3 \), (c) \( \text{NO}_2 \), and (d) \( \text{PM}_{2.5} \) at GCO at the time of the trajectory initialization. The trajectories north of 50\( ^\circ \)N are not shown. For these horizontal trajectories, (e) vertical heights are given.

In episode 2, \( \text{O}_3 \) concentrations were much lower and poorly correlated with those of PAN, compared to episode 1. Instead, PAN was best correlated with \( \text{NO}_2 \) with the highest \( \Delta \text{NO}_2/\Delta \text{PAN} \) among all episodes (Fig. 5a, b). In this case, air masses passed through the Korean Peninsula, carrying low \( \text{O}_3 \) being titrated by high \( \text{NO}_x \) (Brasseur et al., 1999; Jacobson, 2005). These two episodes illustrate the export of urban plumes in northeast Asia region, which are distinguished by the relative enhancement of reactive gases including \( \text{O}_3 \), PAN, and \( \text{NO}_x \), depending on the origin and aging of air masses.

4.3 PAN enhancement upon the occurrence of haze (episodes 3 and 4)

In this study, two haze events were observed in the very beginning (20–21 October; episode 3) and the end of the study period (4–5 November; episode 4). As the nighttime \( \text{O}_3 \) peak
was attributed to the transport from nearby urban areas to Jeju Island, the two haze episodes were also observed in association with continental outflows. The first haze event occurred on 18 October and persisted until 21 October, during which O$_3$ concentrations were gradually elevated. A second peak was recorded around midnight of 19 and 20 October, and the maximum was reached in the afternoon of 20 October (Figs. 1 and 3). In this episode, the maximum concentrations of O$_3$ and PAN were 78.9 and 2.0 ppbv, respectively, on 20 October, when the highest NO$_2$ concentration (12.7 ppbv) was observed under low wind speed (6.6 m s$^{-1}$ daily average). The air mass trajectories suggest the influence of the Korean Peninsula, particularly the Seoul metropolitan area, in addition to east China (Fig. 4).

In the second haze event (episode 4), an air mass was slowly transported from east China, including the Jiangsu province, under stagnant conditions which were developed by an anticyclone system (Fig. 4). We measured the highest concentrations of all aerosol species including the PM$_{2.5}$ mass as well as PAN and O$_3$, which were 156 µg m$^{-3}$, 2.4 ppbv and 87.5 ppbv, respectively. Other reactive gases such as CO, SO$_2$, and NO$_2$ were also highly elevated. Note that PAN and O$_3$ gradually increased through the night, leading to a nighttime maximum of both species on 4 November. It is likely that the pre-formed PAN and O$_3$ were continuously transported into Gosan at night.

PAN is formed through the reaction of the peroxyacetyl radical and nitrogen dioxide (Eq. 1) and decomposed at high temperature (Eq. 2), returning these radicals. Unless the NO concentration is high (Eq. 3), the peroxyacetyl radical recombines with NO$_2$, producing PAN. Thus, the total lifetime of PAN depends on the NO$_2$ / NO ratio and temperature (Eq. 4) (Brasseur et al., 1999).

\[
\begin{align*}
\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{NO}_2 + \text{M} &\rightarrow \text{PAN} + \text{M}, \\
\text{PAN} &\rightarrow \text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{NO}_2, \\
\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{NO} &\rightarrow \text{CH}_3\text{CO}_2 + \text{NO}_2,
\end{align*}
\]

\[
T_{\text{eff}} = T_0 \left(1 + \frac{k_1 [\text{NO}_2]}{k_2 [\text{NO}] } \right) [\text{s}^{-1}],
\]

where $T_0$ and $T_{\text{eff}}$ indicate the lifetime against decomposition and the effective lifetime of PAN (Brasseur et al., 1999).

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Figure 5. Correlations between (a) PAN and O$_3$ and (b) PAN and NO$_2$ with linear regression line for each episode. Correlations between O$_3$ and PAN were color-coded by the level of (c) NO$_2$ and (d) PM$_{2.5}$.

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Figure 6. Correlations among PAN, the $K^+$ ion of PM$_{1.0}$, and carbonaceous components of PM$_{2.5}$ for four episodes: (a) PAN and PM$_{2.5}$ mass, (b) PAN and PM$_{2.5}$ OC, (c) PM$_{2.5}$ EC and OC, and (d) PAN and PM$_{1.0}$ $K^+$. The lines represent the linear regression for each episode.

The effective lifetime of PAN was estimated through Eq. (4) using the rate constants proposed by Brasseur et al. (1999), Jacobson (2005), and Maricq and Szenté (1996). During the haze event, NO was close to the detection limit, while NO$_2$ was greatly enhanced. Owing to the high NO$_2$/NO ratio, the effective lifetime of PAN increased by 57 ± 14 times; this possibly contributed to the gradual increase in PAN through the night on 4 November. For this estimation, the PAN concentration was subtracted from the measured NO$_2$ concentration, considering the positive artifact from the molybdenum converter in the NO$_2$ measurement. Fischer et al. (2014) also reported that, at night, PAN can be produced from the reaction of acetaldehyde with the nitrate radical.

Besides PM$_{2.5}$ mass, PAN was also well correlated with PM$_{2.5}$ OC and EC not only during this haze episode but also during the entire measurement period (Fig. 6a and b). Furthermore, the enhancement of PAN was concurrent with that of OC and K$^+$, resulting in excellent correlation between them (Fig. 6b and d). In fact, the $\Delta$OC/$\Delta$EC ratio of episode 4 was much higher (7) than those of the other episodes (~2.5) (Fig. 6c). The fraction of PM$_{2.5}$ against PM$_{1.0}$ was also the highest in this episode, indicating a significant contribution of secondary aerosols. These observations suggest that air masses were affected by biomass combustion (e.g., Ram et al., 2008, 2012; Saarikoski et al., 2008).

According to previous studies, PAN can be produced in plumes through biomass combustion (Alvarado et al., 2010; Coheur et al., 2007; X. Liu et al., 2016; Tereszchuk et al., 2013). In northeast China, open burnings related to agricultural activities frequently occur during the spring and fall (Duan et al., 2004; Yang et al., 2005). Kudo et al. (2014) also reported that, after the burning of crop residue in the Yangtze region, the levels of oxygenated VOCs were elevated together with NO$_x$. In addition, biofuel is used for cooking and heating and as an energy source in China’s industry (Cao et al., 2006).
Therefore, PAN is likely to increase when haze occurs and fine aerosols are transformed as air masses carrying combustion emissions are slowly transported from China over the Yellow Sea. Additionally, the results of this study imply that PAN can be used as a robust tracer for continental outflows in northeast Asia, to identify transport- and chemical-transformation-dominant regimes. In a transport-dominant regime, fine aerosol species were enhanced regime, O\textsubscript{3} transformation-dominant regimes. In a transport-dominant flow, PAN was well captured (Fig. 7). The elevated PAN concentration was underestimated in the model (20–21 October) when the air masses were affected by urban emissions from Korean Peninsula. Although the maximum O\textsubscript{3} level was lower during episode 2, these two cases demonstrated well how O\textsubscript{3} was exported from the East Asian continent.

Finally, the measured O\textsubscript{3} and PAN concentrations were compared to results from a global chemistry model CAM-chem. In the model simulation, O\textsubscript{3} and PAN were highly underestimated during the episodes observed in Chinese outflows, although the variation around the average level of O\textsubscript{3} and PAN was well captured (Fig. 7). The elevated PAN concentration was underestimated in the model (20–21 October and 4–5 November), especially when air was impacted by biomass combustion. The timing of the O\textsubscript{3} diurnal variability was captured by the model, although the magnitude of the variation was underestimated. These results reveal that the current understanding of Chinese outflow is still not sufficient, thereby causing uncertainty in estimating its effect on air quality in the northwestern Pacific Rim.

5 Conclusions

The first measurements of PAN, reactive gases, and aerosol species were conducted at GCO during 19 October to 6 November 2010. The average concentration of PAN was 0.6 ppbv with a maximum of 2.4 ppbv, which was lower than those in major cities in East Asia but much higher than the background concentrations in other regions. Although the hourly concentrations of PAN and O\textsubscript{3} were well correlated ($\gamma = 0.67$), the comparison of the daily maxima of PAN and O\textsubscript{3} highlighted that they were not proportionally enhanced. That is, either PAN was relatively more elevated than O\textsubscript{3} or the highest O\textsubscript{3} was associated with low levels of PAN. Unexpectedly, both PAN and O\textsubscript{3} often reached their maxima at night. In this study, these high concentrations were all encountered in association with continental outflows, where PAN was decoupled from O\textsubscript{3} and better correlated with the PM\textsubscript{2.5} mass ($\gamma = 0.79$) than with O\textsubscript{3}. Thus, two high-O\textsubscript{3} and two high-PAN events were the most clearly distinguished and investigated in detail.

During the O\textsubscript{3} episodes, both O\textsubscript{3} and PAN concentrations reached their maximum values at night. In episode 1 (31 October to 2 November), the O\textsubscript{3} concentration was increased to 80.6 ppbv, with a high SO\textsubscript{2} concentration under strong wind. This was typical for the Beijing plume observed in the study region. In comparison, NO\textsubscript{2} was greatly increased in episode 2 (28–29 October) when the air masses were affected by urban emissions from Korean Peninsula. Although the maximum O\textsubscript{3} level was lower during episode 2, these two cases demonstrated well how O\textsubscript{3} was exported from the East Asian continent.

The remaining two episodes were highlighted by enhanced PAN concentrations and characterized by haze occurrence. During episode 3 (20–21 October), PAN and O\textsubscript{3} concentrations increased by up to 2.0 and 78.9 ppbv, respectively, with high NO\textsubscript{x} levels, probably influenced by emissions from Korea. Episode 4 (4–5 November) was characterized by the highest concentrations of almost all measured species, including PAN, O\textsubscript{3}, PM\textsubscript{2.5} mass, and PM\textsubscript{1.0} species; the maximum recorded concentrations of PAN, O\textsubscript{3}, and PM\textsubscript{2.5} mass during this interval were 2.4 ppbv, 87.5 ppbv, and 156 µg m\textsuperscript{-3}, respectively. Note that, along with PM\textsubscript{2.5} and O\textsubscript{3}, PAN gradually increased through the night. In this episode, an air mass was slowly transported from eastern China. With depleted NO, the effective lifetime of PAN was greatly extended. In addition, PAN concentration showed good correlation with OC, EC, and K\textsuperscript{+}; in fact, the correlation of PAN with K\textsuperscript{+} was comparable to that of OC with K\textsuperscript{+}. These results, in conjunction with the high OC/EC (7), imply that the observed haze was mainly caused by the emissions produced by biomass combustion. These results suggest that PAN is a useful tool for distinguishing between continental outflows that were typically observed in northeast Asia.
The comparison between the measured and calculated concentrations using the CAM-chem-HTAP2 model showed that the model underestimated the O₃ and PAN levels in Chinese outflows, particularly for haze incidence. These results reveal that Chinese outflows are still poorly understood and not well captured in the model.

Data availability. The data presented in this article are available from the corresponding author upon request.

Competing interests. The authors declare that they have no conflict of interest.

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