Comments to the Author:

The authors have addressed all comments. At this point, there is only minor editorial work remaining, as follows.

We thank the reviewer for his/her further comments on the improvement of the manuscript.

Throughout manuscript: change “foot” of the mountain with “base” and re-assess the use of “due to” throughout the manuscript.

Reply: Thanks for the comment. The “foot” of the mountain has been changed with “base” throughout the whole manuscript. For details, please refer to Line 3 Page 2, Lines 10 and 26 Page 5, Line 15 Page 24, Line 9 Page 26 and Line 4 Page 30 in the revised manuscript.

Furthermore, the use of “due to” has been re-assessed and revised accordingly throughout the manuscript, in addition to those suggested in the following specific comments. For details, please refer to Line 16 Page 2, Lines 3 and 6 Page 3, Lines 7 and 18 Page 6, Line 9 Page 11, Line 22 Page 14, Line 13 Page 19, Lines 15 and 18 Page 20, Line 26 Page 23, Line 14 Page 25, and Line 24 Page 26 in the revised manuscript.

P2L2-3: remove the “i.e.,” before the site names – not needed.

Reply: Thanks for the comment. The text has been deleted as suggested. For details, please refer to Lines 2-3, Page 2 in the revised manuscript.

P2L15: Revise the following sentence “On the other hand, alkyl nitrates at TMS were...” to something like the following: "In contrast to TW, the alkyl nitrate levels measured at TMS mainly resulted from the photo-oxidation of the parent hydrocarbons at TW during mesoscale circulation, i.e., valley breezes, corresponding to 52-86% of the alkyl nitrate levels at TMS.”

Reply: The sentence has been revised as above. Please refer to Lines 15-18, Page 2 in the revised manuscript for details.

P3L2: change “due to” to “because of”

Reply: Thanks for the comment. “Due to” has been revised as “because of”. For details, please refer to Line 3, Page 3 in the revised manuscript.

P3L6: change “due to” to something like “resulting from”

Reply: Thanks for the comment. “Due to” has been revised as “resulting from”. For details, please refer to Line 6, Page 3 in the revised manuscript.

P5L18: delete “i.e.,” not needed – add comma after (TMS)

Reply: Thanks for the comment. The “i.e.,” has been deleted as suggested. For details, please refer to Line 19 Page 5 in the revised manuscript.
P5L28: You state that the monitoring site was 15-20 m above the ground – that's a pretty significant range. Is there more concise information either about the station/inlet height to narrow down this range?

Reply: Thanks for the comment. The monitoring site was approximately 20 m above ground level. The text has been revised accordingly. For details, please refer to Line 30, Page 5 in the revised manuscript.

P8L1: Please introduce CO, NO, NO\textsubscript{2} and NO\textsubscript{x} – this is the first time these have been presented in the manuscript.

Reply: Thanks for the comment. The detailed information of CO, NO, NO\textsubscript{2} and NO\textsubscript{x} has been provided. For details, please refer to Lines 1-2, Page 8 in the revised manuscript.

P8L6: “baseline” should be change to “background”

Reply: “baseline” has been changed to “background”. For details, please refer to Line 9, Page 8 in the revised manuscript.

P8L10-16: The following sentence is confusing – first off how often were each of the different analyzers calibrated? Regarding the “other” analyzers, it says they were calibrated “daily” using scrubbed ambient air – this would be zeroed, not calibrated. The way this is written, the “other” analyzers are only calibrated weekly, but zeroed daily, and we are not provided the information on the temporal calibrations of the ozone analyzer. Please revise to state the frequency of the zeros and calibrations for each of the instruments. The O3 analyzer was calibrated (how often, hourly, daily, weekly?) by using a transfer standard (Thermo Environmental Instruments (TEI) 49PS), while the other analyzers were calibrated daily by analyzing scrubbed ambient air (this is zeroing the analyzer) (TEI, Model 111) and a span gas mixture weekly with a NIST (National Institute of Standards and Technology) traceable standard which was diluted to representative mixing ratios using a dynamic calibrator (Environics, Inc., Model 15 6100).

Reply: Thanks for the comment. The above sentences have been revised as follows:

“The O\textsubscript{3} analyzer was calibrated weekly by using a transfer standard (Thermo Environmental Instruments (TEI) 49 PS), while the other analyzers were zeroed daily by analyzing scrubbed ambient air and calibrated weekly by a span gas mixture with a NIST (National Institute of Standards and Technology) traceable standard which was diluted to representative mixing ratios using a dynamic calibrator (Environics, Inc., Model 6100).”

For details, please refer to Lines 13-18, Page 8 in the revised manuscript.

P9L17: It’s hard to tell in the pdf version, but this should be the beginning of a new paragraph.

Reply: Sorry for the confusion. Indeed, it was the beginning of a new paragraph.
paragraph in the manuscript (in word version). For details, please refer to Line 20 Page 9 in the revised manuscript. To make it clearer, 2 characters were indented for the first line of each paragraph throughout the manuscript.

P12 Table 1 (and also S1): it would be useful to either include 10th and 90th percentiles or quartiles (or both) to the statistics – this allows the reader to better assess the variability in the data and between sites.

Reply: Thanks for the great comment. 10th and 90th percentiles for the data have been added in Table 1 and Table S1. For details, please refer to Table 1 in the revised manuscript and Table S1 in the revised supplementary.

P13L19-21: Revise to the following: High mixing ratios of O3 and alkyl nitrates were usually associated with meteorological conditions with high-pressure system and/or stable conditions, such as high temperatures, intense solar radiation and low wind speeds.

Reply: Thanks for the comment. The sentence has been revised accordingly. For details, please refer to Lines 24-27, Page 13 in the revised manuscript.

P13L27: delete “well” The maximum values were comparable and the diurnal patterns well tracked each...

Reply: It has been deleted. For details, please refer to Line 4, Page 14 in the revised manuscript.

P14L1: add “the” other for the C3-C4 alkyl nitrates...

Reply: The word has been added in the revised manuscript. Please refer to Line 5, Page 14 in the revised manuscript.

P14L5: delete “respectively”

Reply: The word has been deleted in the revised manuscript. Please refer to Line 9, Page 14 in the revised manuscript.

P14L6: simply say “high O3 days” so the sentence reads more fluidly (not high-level)

Reply: The text has been revised accordingly. Please refer to Line 10, Page 14 in the revised manuscript.

P14L19: States that the elevated levels of MeONO2 and EtONO2 are “likely indicative of photo-oxidation of methane and ethane”. Please provide an estimate on this point as the lifetime of methane and ethane are sufficiently long that local production usually isn’t dominate for these two gases.

Reply: Thanks for pointing this out. The high levels of MeONO2 and EtONO2 observed at around noon were likely resulted from regional transport and/or mesoscale circulation, which were further analyzed in Section 3.2.3. Therefore, the text has been revised as follows:
…”likely resulted from regional transport (Guo et al., 2009; Jiang et al., 2010) and/or mesoscale circulations (Gao et al., 2005; Wang et al., 2006) (Section 3.2.3)”
For details, please refer to Lines 23-24, Page 14 in the revised manuscript.

P14L26: Revise this to say that “…the high levels of MeONO2 and EtONO2 are likely related to marine…”
Reply: Thanks for the comment. The text has been revised as suggested. For details, please refer to Line 29, Page 14 in the revised manuscript.

P16L6: replace “helpful” with “valuable”
Reply: “helpful” has been replaced by “valuable”. For details, please refer to Line 9, Page 16 in the revised manuscript.

P16L21: Introduce Eq. 1 – currently, it simply resides in the text with no reference to it.
Reply: Thanks for pointing this out. “Eq.1” has been revised as “Equation 1”. For details, please refer to Line 24, Page 16 in the revised manuscript.

P16L26: revise to “…processing, respectively; [OH] is the…”
Reply: The text has been revised as above. For details, please refer to Line 29, Page 16 in the revised manuscript.

P17L8: delete “most”
Reply: The text has been deleted. For details, please refer to Line 10, Page 17 in the revised manuscript.

P17L17: Delete “[OH]”: The diurnal average OH mixing ratios [OH] were
Reply: The text has been deleted. For details, please refer to Line 20, Page 17 in the revised manuscript.

P17,L20: Revise to: “…because the other parameters (kA, kB, α1, α2 and JRONO2) were obtained from the literatures…” Note: literature should not be plural.
Reply: Thanks for the comment. The “literatures” has been revised as “literature”. For details, please refer to Line 23, Page 17 in the revised manuscript.

P19L13-18: First, the following should be revised: “…due to long atmospheric lifetimes and slow photochemical degradation rates of methane and ethane…” to something as: “…resulting from their relatively long atmospheric lifetimes and the slow photochemical reaction rates of methane and ethane…”
Moreover, this goes back to P14L19, which suggested that the elevated MeONO2 and EtONO2 are a result of photochemistry – these sections can be
construed as contradictory. Please reconcile the discussion on P14 by including a calculation or revising the text accordingly.

Reply: Thanks for the comment. The text “...due to long atmospheric lifetimes and slow photochemical degradation rates of methane and ethane...” has been revised as suggested. For details, please refer to Lines 13-14, Page 19 in the revised manuscript.

Furthermore, the discussion on P14 has been revised as mentioned above (Lines 23-24, Page 14).

P20,L3: Change to “Regarding the C3 alkyl nitrates,...”

Reply: The text has been changed to “Regarding the C3 alkyl nitrates”. For details, please refer to Line 3, Page 20 in the revised manuscript.

P20L5: “revealing” isn’t a great word choice in this case. Recommend changing to something like: indicating, demonstrating, etc.

Reply: The “revealing” has been changed to “indicating”. For details, please refer to Line 5, Page 20 in the revised manuscript.

P21L25-26: Revise to: “The standard error in Figure 7 were...” Note: error should not be plural.

Reply: Thanks for the comment. The text has been revised as “The standard error in Figure 7 was...”. For details, please refer to Lines 25-26, Page 21 in the revised manuscript.

P21L26-29: Revise the following: Since the air masses arriving at TMS were photochemically aged (Guo et al., 2013a), the original source profiles of alkyl nitrates and their parent hydrocarbons were altered at this mountain site.” to something like: “The source profiles of the alkyl nitrates and their parent hydrocarbons were altered resulting from photochemical transformation during transport to the TMS site.”

Reply: Thanks for the comment. The sentence has been revised as above. For details, please refer to Lines 26-28, Page 21.

P22L2, 8 & 15: change n/i-butane to i/n-butane to be consistent throughout the manuscript.

Reply: Thanks for pointing this out. All the “n/i-butane” has been corrected as “i/n-butane” throughout the manuscript.

P24L16: As written, this refers to a single forest fire – is this correct or should this be plural?

Reply: Yes, the fire should be plural. The text has been revised accordingly. For details, please refer to Line 16, Page 24 in the revised manuscript.
P26L1: Delete “Instead” and start the sentence with “The C3-C4...” or say something such as: “In contrast to the C1 and C2 alkyl nitrates,...”

Reply: The text has been revised as suggested. For details, please refer to Line 1, Page 26 in the revised manuscript.

P26L8: Replace “brought” with “transported”

Reply: “brought” has been replaced by “transported”. For details, please refer to Line 8, Page 26 in the revised manuscript.

P26L22-23: for the following: “...photochemical formation of alkyl nitrates was occurring, and eventually contributed to the ambient levels of alkyl nitrates at TMS.” either delete the part of the sentence after the comma or revise as follows: “...photochemical formation of alkyl nitrates was occurring, contributing to their ambient levels at TMS.”

Reply: Thanks for the comment. The sentence has been revised as “...contributing to their ambient levels at TMS”.
For details, please refer to Lines 22-23, Page 26 in the revised manuscript.

P27L4-8: For the following: The results demonstrated that when there was mesoscale circulation, the levels of alkyl nitrates at TMS were dominated by the photo-oxidation of their parent hydrocarbons originated from the urban site TW, one possible reason leading to similar levels of alkyl nitrates at the two sites, though the values of their parent hydrocarbons were lower at TMS. Revise to something like: These results demonstrate that when there was mesoscale circulation, the alkyl nitrate levels at TMS were dominated by the photo-oxidation of their parent hydrocarbons that originated from the urban site TW. Although the mixing ratios of the parent hydrocarbons were lower at TMS, this is still one possible explanation leading to the similar levels of alkyl nitrates measured at the two sites.

Reply: Thanks for the comment. The sentence has been revised as follows: “These results demonstrate that when there was mesoscale circulation, the alkyl nitrate levels at TMS were dominated by the photo-oxidation of their parent hydrocarbons that originated from the urban site TW. Although the mixing ratios of the parent hydrocarbons were lower at TMS, this is still one possible explanation leading to the similar levels of alkyl nitrates measured at the two sites.”
For details, please refer to Lines 4-9, Page 27 in the revised manuscript.

P27L24: change to “...alkyl nitrates measured at TMS.”

Reply: The text has been revised accordingly. For details, please refer to Line 25, Page 27 in the revised manuscript.

P27L26: change “...in the...” to “...for the...”

Reply: “in” has been changed to “for”. For details, please refer to Line 27,
Page 27 in the revised manuscript.

P28,L20-21: For the following: In addition, as the formation of alkyl nitrates consumes NO, it resulted in negative contribution to O3 formation.
Change to: Additionally, as the formation of alkyl nitrates consumes NO, this process results in a negative contribution to O3 formation.
Reply: The sentence has been revised as suggested above. For details, please refer to Lines 21-22, Page 28 in the revised manuscript.

P29L20: Change: “The results...” to “These results...”
Reply: “The results...” has been revised as “These results...”. For details, please refer to Line 22, Page 29 in the revised manuscript.

P30L19: change “…led to the...” to “…resulted in...”
Reply: “…led to the...” has been changed to “…resulted in...”. For details, please refer to Line 19, Page 30 in the revised manuscript.

Figure S1: Change to sans serif font and adjust the colors so TW is red to be consistent with the rest of the manuscript.
Reply: The reviewer’s comment is highly appreciated. In fact, there was no sans serif font in the software we used to draw the figure, we have changed the font to be “Arial”. Furthermore, to present the figure more clearly, the font size has been increased. Additionally, the colors for TW have been changed to be red. For details, please refer to Figure S1 in the revised supplementary.

Figure S2: Is it possible to increase the clarity of the labels on the weather charts?
Reply: Thanks for the comment. The clarity of the labels on the weather charts has been improved. Please refer to Figure S2 for details.
New insight into the spatiotemporal variability and source apportionments of C$_1$-C$_4$ alkyl nitrates in Hong Kong

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Abstract

C₁-C₄ alkyl nitrates (RONO₂) were measured concurrently at a mountain site, Mt. Tai Mo Shan (TMS), and an urban site, Tsuen Wan (TW) at the base of the same mountain in Hong Kong from September to November 2010. Although the levels of parent hydrocarbons were much lower at TMS (p<0.05), similar alkyl nitrate levels were found at both sites regardless of the elevation difference, suggesting various source contributions of alkyl nitrates at the two sites. Prior to using a positive matrix factorization (PMF) model, the data at TW were divided into “meso” and “non-meso” scenarios for the investigation of source apportionments with the influence of mesoscale circulation and regional transport, respectively. Secondary formation was the prominent contributor of alkyl nitrates in the “meso” scenario (60 ± 2%, 60.2 ± 1.2 pptv), followed by biomass burning and oceanic emissions, while biomass burning and secondary formation made comparable contributions to alkyl nitrates in the “non-meso” scenario, highlighting the strong emissions of biomass burning in the inland Pearl River Delta (PRD) region. In contrast to TW, the alkyl nitrate levels measured at TMS mainly resulted from the photo-oxidation of the parent hydrocarbons at TW during mesoscale circulation, i.e. valley breezes, corresponding to 52-86% of the alkyl nitrate levels at TMS. Furthermore, regional transport from the inland PRD region made significant contributions to the levels of alkyl nitrates (~58-82%) at TMS in the “non-meso” scenario, resulting in similar levels of alkyl nitrates observed at the two sites. The simulation of secondary formation pathways using a photochemical box model found that the reaction of alkyl peroxy radicals (RO₂) with nitric oxide (NO) dominated the formation of RONO₂ at both sites, and the formation of alkyl nitrates contributed negatively to O₃ production, with average reduction rates of 4.1 and 4.7 pptv/pptv at TMS and TW, respectively.

Key word: Alkyl nitrates; Source apportionment; Secondary formation; Biomass burning
1. Introduction

Alkyl nitrates (RONO₂) are important photochemical pollutants in the atmosphere because of their roles in local, regional and global atmospheric chemistry (Jenkin et al., 2000; Seinfeld and Pandis, 2006). Alkyl nitrates are reactive nitrogen compounds (NOₓ) and act as a critical reservoir of nitrogen oxides (NOₓ = NO + NO₂) during long-range transport resulting from their relatively low reactivity (Atkinson, 2006).

A number of studies conducted in different environments have shown that alkyl nitrates are either emitted from marine sources directly and/or produced indirectly through photochemical reactions (Roberts et al., 1998; Blake et al., 2003; Simpson et al., 2002, 2003, 2006; Reeves et al., 2007; Wang et al., 2013). In the case of biomass burning, secondary alkyl nitrate formation is believed to occur by the photo-oxidation of emitted hydrocarbons with a formation mechanism of RO and NO₂ (Simpson et al., 2002). The photochemical pathways for the secondary formation of alkyl nitrates are expressed as follows (Atkinson et al., 2006; Jenkin et al., 2000; Arey et al., 2001; Sommariva et al., 2008):

\[
\begin{align*}
\text{RH} + \text{OH}^- & \rightarrow \text{R}^+ + \text{H}_2\text{O}, \ k_1, \ \alpha_1 \ (R1) \\
\text{R}^+ + \text{O}_2 & \rightarrow \text{RO}_2^-, \ k_2 \ (R2) \\
\text{RO}_2^- + \text{NO} & \rightarrow \text{RO}^- + \text{NO}_2, \ k_3, \ 1-\alpha_2, \ (R3) \\
\text{RO}_2^- + \text{NO} & \rightarrow \text{RONO}_2, \ k_4, \ \alpha_2, \ (R4) \\
\text{RO} + \text{NO}_2 & \rightarrow \text{RONO}_2, \ k_5 \ (R5)
\end{align*}
\]

where \( k_1, k_2, k_3, k_4 \) and \( k_5 \) are reaction rate constants. \( \alpha_1 \) and \( \alpha_2 \) are branching ratios for the corresponding radicals, which increase as the carbon number increases and are dependent on the carbon chain length.

Photochemical formation of alkyl nitrates influences the oxidation of NO to NO₂, subsequently leading to O₃ production by NO₂ photolysis. Therefore, alkyl nitrates are often used as indicators of photochemical O₃ production (Simpson et al., 2006). Furthermore, the interactions of alkyl nitrates with their parent hydrocarbons provide useful information about the photochemical processing of air masses. Comparing measured and predicted RONO₂/RH ratios calculated using the laboratory kinetic data
as a function of time, Bertman et al. (1995) examined the photochemical evolution of alkyl nitrates at Scotia, Pennsylvania and the Kinterbish Wildlife Area, Alabama. Since then, this approach has been used to investigate the evolution of alkyl nitrates with air mass age in different regions (Simpson et al., 2006; Reeves et al., 2007; Russo et al., 2010; Worton et al., 2010; Wang et al., 2013). Fairly good agreement (>0.5) between measured and modeled ratios suggests that the oxidation of single-parent hydrocarbons represents the evolution of their daughter alkyl nitrates, while poor correlation indicated sources other than photochemical formation of alkyl nitrates.

In contrast, the main sinks for ambient alkyl nitrates are photolysis and reactions with hydroxyl radical (OH), making alkyl nitrate lifetimes vary with season, latitude and altitude (days to weeks):

\[
\text{RONO}_2 + h\nu \rightarrow \text{RO}^- + \text{NO}_2, J_{\text{RONO}_2}, (R6)
\]

\[
\text{RONO}_2 + \text{OH}^\cdot \rightarrow \text{products}, k_6, (R7)
\]

where \( h\nu \) is sunlight and \( J_{\text{RONO}_2} \) and \( k_6 \) are the photolysis and OH reaction rate constants, respectively. The importance of alkyl nitrate removal by photolysis decreases as the carbon number increases (Clemitshaw et al., 1997; Talukdar et al., 1997). Dry deposition has recently been recognized as another pathway for the removal of atmospheric alkyl nitrates (Russo et al., 2010; Wu et al., 2011).

Despite increased concern over photochemical pollution in Hong Kong and the greater Pearl River Delta (PRD) region, limited studies have focused on the characteristics of alkyl nitrates, which share a common mechanism with photochemical \( \text{O}_3 \) formation and act as indicators of photochemical processing. For example, based on measurements conducted in 2001-2002, including during ozone episodes, Simpson et al. (2006) analyzed the general characteristics of alkyl nitrates at a coastal site (Tai O) in Hong Kong. \( \text{C}_3-\text{C}_4 \) alkyl nitrates were the most abundant species, with maximum and minimum levels in winter and summer, respectively. The diurnal variations suggested that photochemical production was the dominant source of alkyl nitrates at Tai O. Furthermore, through approximate calculations, it was concluded that the methoxy radical (\( \text{CH}_3\text{O}^- \)) reaction with \( \text{NO}_2 \) was a viable
alternative pathway for the observed high levels of MeONO₂ during pollution episodes. This mechanism was subsequently verified by Archibald et al. (2007) via box model simulations, whereby RO + NO₂ → RONO₂ became important for MeONO₂ formation at 10 ppb NO₂ and dominant at 35 ppb NO₂. However, knowledge related to the chemical evolution and source apportionments of individual alkyl nitrates and their relationship with parent hydrocarbons is still lacking in Hong Kong, especially given that levels of alkyl nitrate precursors have varied since 2002 (Ling and Guo 2014). Hence, in this study, intensive field measurements of C₁-C₄ alkyl nitrates were conducted at two sites - a mountain site (Mt. Tai Mo Shan, TMS) and an urban site (Tsuen Wan, TW) at the base of the same mountain in Hong Kong. The data were analyzed and compared with the previous study conducted at Tai O (Simpson et al., 2006). The aims were to investigate the spatiotemporal variations and, for the first time, source apportionments and photochemical formation pathways and evolution of alkyl nitrates in Hong Kong.

2. Methodology

2.1. Sampling sites

In this study, concurrent field measurements were conducted at two sites located at different elevations of the highest mountain, Mt. Tai Mo Shan (TMS) with an elevation of 957 m a.s.l. in Hong Kong from September 6 to November 29, 2010. A detailed description of the topography of Mt. TMS was provided in an overview paper (Guo et al., 2013a). In brief, Figure 1 presents the two sampling locations and the surroundings. The high-elevation site (TMS) was set on the rooftop of a building on the mountainside (640 m a.s.l.), the highest logistically feasible observation location, beyond which the area comprised the natural landscape with shrubs and grasses to the mountain summit (AFCD, 2008). The measurement site at the base of the mountain was the monitoring station of the Hong Kong Environmental Protection Department (HKEPD) at Tsuen Wan (TW), a mixed residential, commercial and light industrial area in the New Territories of Hong Kong. The TW monitoring site was located on the rooftop of a building, approximately 20 m above ground level. The linear distance
between the TMS and TW sites was about 7 km and the difference in elevation between the two sites was 630 m. In general, the solar radiation was comparable at the two sites, while the temperature was higher and the relative humidity and wind speed were lower at the TW site (Guo et al., 2013a). The winds at TMS were generally from the north with speeds ranging from 0.02 to 4 m s\(^{-1}\), and the winds at TW were predominantly from the southeast at speeds of 1-3 m s\(^{-1}\) with easterly winds at night and southerly winds during the day. Because of its unique topography, the air at TMS was often influenced by the mountain-valley breezes and regional transport (Guo et al., 2013a). Based on the average wind speed of 1.9 m/s, air masses transported from upwind locations, on both local (~7 km) and regional scales (~20 km), took approximately 1-3 hours to arrive at the TMS site (Guo et al., 2012, 2013a).

The Tai O sampling station was a rural/coastal site located on the western coast of Lantau Island in southwestern Hong Kong (elevation, 80 m a.s.l.) (Figure 1). This site overlooks the Pearl River Estuary to the west and north, and the South China Sea to the south. It is 32 km away from the urban center to the east and about the same distance from Macau/Zhuhai to the west. Major man-made sources in the region are located to the east, north and southwest. Local emissions are small because of a sparse population and light traffic. Owing to Asian Monsoon circulation, this site is frequently affected by polluted continental air masses from the highly industrialized PRD region of mainland China in cold seasons. A detailed description of the site is provided in Wang et al. (2003).

Figure 1. Tai Mo Shan (TMS) and Tsuen Wan (TW) sampling sites and the surrounding environments in Hong Kong.
**2.2. Sampling and analysis of volatile organic compounds (VOCs)**

Whole air samples were collected on 10 O\textsubscript{3} episode days and 10 non-O\textsubscript{3} episode days using evacuated 2-L stainless steel canisters. Each of the collected canister samples was integrated over a 60-min sampling period. A total of 384 samples were collected at the two sites. The O\textsubscript{3} episode days were selected as the days with the highest daytime hourly O\textsubscript{3} level at a regional scale (higher than 100 ppbv), which were based on weather forecasts and meteorological data analysis, and confirmed by the observed O\textsubscript{3} mixing ratios. During non-O\textsubscript{3} episode days, one-hour integrated samples were collected at 2-h intervals from 0700 to 1900 local time (LT) (7 samples per day). On O\textsubscript{3} episode days, one-hour integrated samples were collected from 0900 to 1600 LT at 1-h intervals with additional integrated samples collected at 1800, 2100, 0000, 0300 and 0700 LT (a total of 13 samples per day). After the campaign, the canister samples were sent to the University of California, Irvine (UCI) for chemical analysis. Other studies have provided detailed descriptions of the analytical system and the quality control, detection limits and analysis precision of the VOC samples (Simpson et al., 2006, 2010). In brief, the precision and detection limit of the alkyl nitrate measurements is 5% and 0.02 pptv, respectively. The calibration scale for the alkyl nitrate measurements changed in 2008, increasing by factors of 2.13, 1.81, 1.24 and 1.17 for the C\textsubscript{1}, C\textsubscript{2}, C\textsubscript{3} and C\textsubscript{4} alkyl nitrates, respectively (Simpson et al., 2011). In other words, the alkyl nitrates reported at Tai O by Simpson et al. (2006) were lower than the data reported here, and the Tai O data have been adjusted to the new calibration scale to allow direct comparison with this work. The Tai O sampling campaign was conducted from 24 August 2001 to 31 December 2002. Different from the air samples collected at TMS and TW, each whole-air sample at Tai O was collected for only 1-min, and was then analyzed at UCI. Intensive sampling from 0700-1900 LT was conducted every 2-h during the selected pollution episodes (17-19 October 2001, 29-30 August, 5-6 September, 9-11 and 25 October, 6-8 and 12 November 2002). Apart from the intensive sampling days, samples were taken either daily or every few days, typically in the midafternoon (Simpson et al., 2006).
2.3. Continuous measurements of O$_3$, carbon monoxide (CO) and nitric oxide – nitrogen dioxide – nitrogen oxides (NO-NO$_2$-NO$_x$)

At TMS, online measurements of O$_3$, CO and NO-NO$_2$-NO$_x$ were made using commercial analyzers. Ozone was measured using a commercial UV photometric instrument (Advanced Pollution Instrumentation (API), model 400E) that has a detection limit of 0.6 ppbv. Carbon monoxide was measured with a gas filter correlation, nondispersive infrared analyzer (API, Model 300E) with a heated catalytic scrubber (as purchased) to convert CO to carbon dioxide (CO$_2$) for background determination. The detection limit was 30 ppbv for a 2-min average. The 2σ precision was about 1% for a level of 500 ppbv (2-min average) and the overall uncertainty was estimated to be 10%. NO, NO$_2$ and NO$_x$ were detected with a chemiluminescence NO-NO$_2$-NO$_x$ analyzer (API, Model 200E) that had a detection limit of 0.5 ppbv. The O$_3$ analyzer was calibrated weekly by using a transfer standard (Thermo Environmental Instruments (TEI) 49 PS), while the other analyzers were zeroed daily by analyzing scrubbed ambient air and calibrated weekly by a span gas mixture with a NIST (National Institute of Standards and Technology) traceable standard which was diluted to representative mixing ratios using a dynamic calibrator (Envirronics, Inc., Model 6100). The Standard (Scott-Marrin, Inc.) contained 156.5 ppmv CO (±2%), 15.64 ppmv SO$_2$ (±2%), and 15.55 ppmv NO (±2%). For the O$_3$, CO, NO and NO$_x$ analyzers, a data logger (Environmental Systems Corporation Model 8816) was used to control the calibrations and to collect 1-minute data.

In addition to the above chemical measurements, several meteorological parameters, including wind speed and direction, temperature, relative humidity and solar radiation, were measured by the integrated sensor suite (Vantage Pro TM & Vantage Pro 2 Plus TM Weather Stations, Davis Instruments).

At TW, hourly O$_3$, CO, NO–NO$_2$–NO$_x$ and meteorological data were obtained from the HKEPD (http://epic.epd.gov.hk/ca/uid/airdata). The hourly data were derived by averaging 1-min data subsequently over the same time interval as the TMS data. Detailed information about the measurements, quality assurance and control protocols can be found in the HKEPD report (HKEPD, 2012). In addition, Table S1 in the
supplementary information shows descriptive statistics of main non-methane hydrocarbons (NMHCs) and trace gases at both sites, while Figure S1 presents the time series of trace gases and meteorological parameters at the two sites.

2.4. Positive Matrix Factorization (PMF) model

In this study, the US EPA PMF 3.0 (http://www.epa/heasd/products/pmf/pmf.html) was used for the source apportionments of the observed alkyl nitrates at TW. Our previous studies provided detailed information about the PMF model (Ling et al., 2011; Ling and Guo, 2014). In terms of the PMF input, the uncertainty for each species was determined as the sum of 10% of the VOC concentration and two times the method detection limit (MDL) of the species (Paatero, 2000). Tracers for different sources were selected for the model input. For example, CO, ethane and ethyne were the tracers of combustion processes, and CH₃Cl was specifically used for biomass burning. DMS was a typical tracer for marine emissions, while Oₓ (i.e., O₃ + NO₂) was used as the tracer of secondary formation through photochemical reactions, including the formation of alkyl nitrates, because O₃ shares a common photochemical source with alkyl nitrates (Simpson et al., 2006). In addition to the aforementioned species, alkyl nitrate precursors, including methane, ethane, propane and i/n-butanes, were input into the model. In total, sixteen compounds were used for the model input.

Various checks and sensitivity tests were conducted to examine the model performance. Firstly, many different starting seeds were tested and no multiple solutions were found. Secondly, the correlation between the predicted and measured concentration of each species was fairly good at TW (R²=0.64–0.94) after the PMF implementation. Thirdly, the scale residuals, which are the uncertainty over the different runs for the input species, ranged between −3 and 3 for the PMF solution. Fourthly, the ratios of Q(robust)/Q(true) were close to 1 for 4-factor solution, within the ranges of 0.97-0.98 at TW, higher than those of 3-factor and 5-factor solutions, indicating all data points were fit better in the 4-factor solution. Indeed, the extracted source profiles from the 4-factor solution were the most reasonable. All the factors were mapped to a base factor in all the 100 runs in the bootstrapped simulation for the
four-factor solution, suggesting the solution was stable. Lastly, the G-space plot extracted from the F-peak model results did not present oblique edges, reflecting that there was little rotation for the selected solution. Overall, the above features demonstrated that PMF provided reasonable results for the source apportionment of alky nitrates (Ling et al., 2011; Ling and Guo, 2014).

2.5. Photochemical box model incorporating master chemical mechanism (PBM-MCM)

A photochemical box model coupled with Master Chemical Mechanism (PBM-MCM) was used to simulate the in-situ formation of alkyl nitrates at TMS and TW. The PBM-MCM was developed by assuming that it was a well-mixed box without the treatment of vertical or horizontal dispersion, and the air pollutants in the model were homogeneous. For the mechanism coupled in the model, the MCM (version 3.2) used in this study is a state-of-the-art chemical mechanism, which describes the degradation of 143 primary VOCs including methane and contains around 16,500 reactions involving 5900 chemical species (Jenkin et al., 1997, 2003; Saunders et al., 2003). The measured data, including O₃, CO, NOₓ, SO₂, 54 VOCs and methane, together with the actual meteorological conditions of temperature, relative humidity and boundary layer in the region, were used to constrain the model. The photolysis rates of different species in the model were parameterized as suggested by the previous study (Pinho et al., 2009) using the photon flux determined from the Tropospheric Ultraviolet and Visible Radiation (v5) model based on the actual conditions, such as meteorological conditions, location and time period of the field campaign in Hong Kong (Lam et al., 2013). The model output simulated in-situ formation of alkyl nitrates and other secondary products as well as the full set of precursors, radicals and intermediates. To provide robust results from the model simulation, several measures were adopted for the model development. The detailed information for the model frameworks, the model development and the evaluation for the model performance has been reported in our previous studies (Lam et al., 2013; Ling et al., 2014).
3. Results and discussion

3.1 Descriptive statistics of alkyl nitrates and their parent hydrocarbons

Table 1 presents the descriptive statistics of alkyl nitrates and their parent hydrocarbons at TMS and TW. Figure 2 compares the levels of alkyl nitrates measured at TMS and TW with those measured in different environments in previous studies. In general, 2-PrONO$_2$ and 2-BuONO$_2$ were the most abundant alkyl nitrates at the two sites, consistent with the results observed in different environments (Blake et al., 2003; Simpson et al., 2006; Russo et al., 2010; Wang et al., 2013). The relatively higher levels of 2-PrONO$_2$ and 2-BuONO$_2$ were associated with the balance between increased branching ratios for photochemical alkyl nitrate formation and the decreased lifetime of both parent alkanes and alkyl nitrates with increasing carbon number (Arey et al., 2001; Simpson et al., 2006; Russo et al., 2010). In comparison, the levels of MeONO$_2$, EtONO$_2$ and 1-PrONO$_2$ were slightly higher at TW than at TMS ($p < 0.05$), with average values of 12.6 ± 0.5 (mean ± 95% confidence interval), 13.3 ± 0.6 and 26.3 ± 1.2 pptv, respectively, at TW. The average mixing ratios of 1-PrONO$_2$ and 2-BuONO$_2$ were comparable at the two sites ($p > 0.05$). The results were contradictory to the fact that the mixing ratios of their parent hydrocarbons at TMS were much lower than at TW, highlighting the complexity of sources of alkyl nitrates at both sites.

In comparison with other studies, the average mixing ratios of alkyl nitrates at TMS were much higher than those measured in forested areas in coastal New England (Russo et al., 2010) and in tropospheric air influenced by Asian outflow during the airborne TRACE-P mission (Simpson et al., 2003), where the levels of parent hydrocarbons were also lower. (Note that all of the UCI data shown in Figure 2 were adjusted to UCI’s post-2008 alkyl nitrates’ calibration scale to enable direct comparison (Simpson et al., 2011). However, the mean mixing ratios of C$_1$-C$_3$ alkyl nitrates were slightly lower and the 2-BuONO$_2$ mixing ratio was higher at TMS than at Tai O (Table 2), Hok Tsui and in Karachi, Pakistan (Barletta et al., 2002; the Karachi data have also been adjusted to the new UCI alkyl nitrates’ calibration scale). The differences among TMS, Tai O and Hok Tsui might result not only from the
levels of their parent hydrocarbons, but also from the influence of air masses with different photochemical ages and sources (Wang et al., 2003). Furthermore, as mentioned in Section 2.2, the sampling method and sampling period at TMS were different from those at Tai O and Hok Tsui, where the sampling duration was only 1-min and the sampling time varied on different sampling days. In particular, many whole air samples were collected during O3 episodes at Tai O. These could also induce differences in observed levels among the three sites. At the urban TW site, the mean mixing ratios of alkyl nitrates were lower than those measured in urban areas in Europe (Worton et al., 2010) and China (Wang et al., 2013). Compared to the average values of alkyl nitrates at Tai O, the levels of EtONO2, 1-PrONO2 and 2-BuONO2 were slightly higher and the MeONO2 and 2-PrONO2 mixing ratio was lower at TW.

Table 1 Descriptive statistics of alkyl nitrates and parent hydrocarbons (pptv) in whole air samples collected at TMS and TW during the sampling period.

<table>
<thead>
<tr>
<th>Species</th>
<th>TMS</th>
<th>TW</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean* 10\text{th} 90\text{th}</td>
<td>Mean 10\text{th} 90\text{th}</td>
</tr>
<tr>
<td>MeONO2</td>
<td>10.9±0.4 6.2 21.4 8.1 13.6 12.6±0.5 7.2 26.6 9.2 16.4</td>
<td></td>
</tr>
<tr>
<td>EtONO2</td>
<td>12.1±0.5 3.2 25.6 7.6 16.5 13.3±0.6 4.0 35.0 8.3 18.1</td>
<td></td>
</tr>
<tr>
<td>2-PrONO2</td>
<td>24.1±1.1 4.0 51.2 14.8 34.7 26.3±1.2 6.0 49.2 16.2 36.2</td>
<td></td>
</tr>
<tr>
<td>1-PrONO2</td>
<td>3.8±0.2 0.4 10.6 1.9 5.5 4.0±0.2 0.7 8.1 2.2 6.1</td>
<td></td>
</tr>
<tr>
<td>2-BuONO2</td>
<td>32.0±1.7 3.1 80.1 18.8 46.6 34.2±1.9 5.1 92.8 20.8 49.2</td>
<td></td>
</tr>
<tr>
<td>Methane (ppmv)</td>
<td>2.0±0.1 1.8 2.2 1.9 2.0 2.0±0.1 1.8 2.5 1.9 2.0</td>
<td></td>
</tr>
<tr>
<td>Ethane</td>
<td>1908±78 396 3588 1154 2470 2224±90 717 4315 1359 2906</td>
<td></td>
</tr>
<tr>
<td>Propane</td>
<td>1101±75 106 4455 569 1749 3551±415 1443 33800 1844 5153</td>
<td></td>
</tr>
<tr>
<td>n-Butane</td>
<td>830±91 97 6252 349 1517 4486±482 1372 34700 2168 7633</td>
<td></td>
</tr>
</tbody>
</table>

* Average ± 95% confidence interval
* 10\text{th} and 90\text{th} percentiles
Figure 2. Comparison of alkyl nitrate mixing ratios in different locations. Data collected by UCI before 2008 (PRD and TRACE-P) were adjusted to UCI’s new calibration scale to permit direct comparison (see text for details about the new calibration).


Table 2 Descriptive statistics of alkyl nitrate (pptv) and parent hydrocarbons (ppbv) in whole air samples collected at Tai O between 24 August 2001 and 31 December 2002 (from Simpson et al., 2006).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Median</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeONO₂</td>
<td>5.5</td>
<td>52.2</td>
<td>13.4</td>
<td>15.9</td>
</tr>
<tr>
<td>EtONO₂</td>
<td>2.7</td>
<td>34.3</td>
<td>12.1</td>
<td>13.1</td>
</tr>
<tr>
<td>1-PrONO₂</td>
<td>0.2</td>
<td>14.5</td>
<td>3.5</td>
<td>3.9</td>
</tr>
<tr>
<td>2-PrONO₂</td>
<td>2.4</td>
<td>65.9</td>
<td>24.5</td>
<td>32.6</td>
</tr>
<tr>
<td>2-BuONO₂</td>
<td>0.8</td>
<td>89.8</td>
<td>27.4</td>
<td>30.7</td>
</tr>
<tr>
<td>Methane (ppmv)</td>
<td>1.75</td>
<td>3.70</td>
<td>1.96</td>
<td>2.05</td>
</tr>
<tr>
<td>Ethane (ppbv)</td>
<td>0.38</td>
<td>5.05</td>
<td>2.14</td>
<td>2.12</td>
</tr>
<tr>
<td>Propane (ppbv)</td>
<td>0.006</td>
<td>13.0</td>
<td>1.54</td>
<td>2.05</td>
</tr>
<tr>
<td>n-Butane (ppbv)</td>
<td>0.006</td>
<td>12.8</td>
<td>0.95</td>
<td>1.64</td>
</tr>
</tbody>
</table>

Table S2 and Figure S2 in the supplementary information summarize the synoptic weather conditions and the corresponding variations of O₃ and alkyl nitrates on O₃ episode and non-O₃ episode days at both sites. In general, meteorological conditions including temperatures, winds and solar radiation significantly influenced the levels of air pollutants (Table S2). High mixing ratios of O₃ and alkyl nitrates were usually associated with meteorological conditions with high-pressure system and/or stable conditions, such as high temperatures, intense solar radiation and low wind speeds. Figure 3 shows the time series of C₁-C₄ alkyl nitrates on O₃ episode and non-O₃ episode days at both sites, while Figure 4 presents the temporal variations of...
their parent hydrocarbons accordingly. Although the ranges of alkyl nitrate mixing ratios were similar and maximum values were observed in the afternoon, the day-to-day variations of individual alkyl nitrates differed during the sampling period at both sites. The maximum values were comparable and the diurnal patterns tracked each other for the C3-C4 alkyl nitrates at TMS and TW, especially on the days (24 October to 3 November, 9 and 19 November) with relatively higher O3 mixing ratios (p < 0.05). The average daytime O3 mixing ratios (0700-1800) on the high O3 days were 77 ± 3 and 38 ± 3 ppbv at TMS and TW, respectively, compared to 58 ± 3 and 23 ± 3 ppbv, on the non-O3 episode days. Typically, the average daytime levels of 2-PrONO2, 1-PrONO2 and 2-BuONO2 on high O3 days at TMS were 27 ± 1 (TW: 28 ± 1), 4.5 ± 0.3 (4.4 ± 0.2) and 37 ± 2 (39 ± 3) pptv, respectively, higher than those on non-O3 episode days (p < 0.05), implying that secondary formation of alkyl nitrates might be more prominent on O3 episode days. Coincident with the high C3-C4 alkyl nitrates during high O3 days, their parent hydrocarbons, i.e., propane (0.56-4.46 and 1.55-10.4 ppbv for TMS and TW, respectively) and n-butane (0.28-6.25 and 1.47-16.1 ppbv, respectively) also showed elevated mixing ratios (Figure 4), further suggesting an important source of C3-C4 alkyl nitrates which was photo-oxidation of the parent hydrocarbons. For the C1-C2 alkyl nitrates, the temporal patterns of MeONO2 and EtONO2 were different at the two sites, especially on high-level O3 days. The peaks of MeONO2 and EtONO2 were usually observed between 11 a.m. and 4 p.m. at TMS, except for 14 and 28 October, 1-2, 9, 20-21 November. The peaks of C1-C2 alkyl nitrates corresponded to the high levels of methane and ethane observed at 11 a.m. to 5 p.m., likely resulted from regional transport (Guo et al., 2009; Jiang et al., 2010) and/or mesoscale circulations (Gao et al., 2005; Wang et al., 2006) (Section 3.2.3). At TW, however, besides the maximum concentrations observed in the afternoon, high levels of MeONO2 and EtONO2 were observed from midnight to early morning on 13 out of the 19 sampling days (i.e., 2, 8, 14, 24, 28, 30-31 October, 1-3, 19-21 November), when the prevailing winds switched to the southeast direction, implying that the high levels of MeONO2 and EtONO2 are likely related to marine emissions and aged continental plumes which were re-circulated from the South China Sea to
the coastal urban site at night. Indeed, this speculation was supported by the source apportionment results at TW, which confirmed that the high MeONO₂ and EtONO₂ levels from midnight to early morning on the above sampling days were related to oceanic emissions (see Section 3.2.2 for details).

![Figure 3](image1.png)

Figure 3. Time series of MeONO₂, EtONO₂, 1-PrONO₂, 2-PrONO₂ and 2-BuONO₂ measured at TMS (purple) and TW (red) in 2010. The yellow shading highlights the O₃ episode days.

![Figure 4](image2.png)

Figure 4. Time series of the parent hydrocarbons of alkyl nitrates at TMS and TW. The yellow shading highlights the O₃ episode days.

Although the levels of the parent hydrocarbons were lower at TMS, similar
values of alkyl nitrates were observed at both sites, regardless of the elevation, suggesting the contributions of different sources and/or the influences of different air masses. Hence, the source apportionments of alkyl nitrates, contributions of reaction pathways for the secondary formation of alkyl nitrates, and the relationship between O$_3$ and alkyl nitrates were analyzed in the following sections.

3.2. Sources of alkyl nitrates

3.2.1. Photochemical evolution of alkyl nitrates

As photochemical oxidation of parent hydrocarbons is an important source of alkyl nitrates, it is valuable to study the photochemical evolution of alkyl nitrates. To do so, the relationships of alkyl nitrates with their parent hydrocarbons at the two sites were further examined using a simplified sequential reaction model developed by Bertman et al. (1995) (Equation 1), based on the assumptions that: (i) the hydrogen abstraction reaction from the parent hydrocarbon was the rate-limiting step for photochemical production of alkyl nitrates, and (ii) the reaction environment was NO$_x$-rich, making the reaction with NO being the dominant pathway for the removal of RO$_2$ radicals (Russo et al., 2010). In this study, the average mixing ratios of NO$_x$ at TMS and TW were 10.7 ± 0.3 and 56.3 ± 1.6 ppbv, respectively, indicating that the environment was NO$_x$-rich (> 0.1 ppbv, Roberts et al., 1998). Hence, reaction with NO was the main pathway for the removal of RO$_2$ radicals at the two sites. In addition, the results of PBM-MCM model simulation confirmed that the hydrogen abstraction reaction from the parent hydrocarbon, namely the reaction of hydrocarbon with OH radical, was indeed the rate-limiting step for photochemical production of alkyl nitrates at both sites (Lyu et al., 2015).

\[
\frac{RONO_2}{RH} = \frac{\beta k_A}{k_B - k_A} \left(1 - e^{(k_A - k_B)t}\right) + \frac{[RONO_2]_0}{[RH]_0} e^{(k_A - k_B)t} \quad \text{(Equation 1)}
\]

where $\beta = a_1a_2$, $k_A$ is the production rate for the formation of alkyl nitrates through the oxidation of hydrocarbons, RH ($k_A = k_1[OH]$), while $k_B$ is the destruction rate for alkyl nitrates through photolysis and the reaction with OH ($k_B = k_5[OH] + J_{RONO2}$). [RONO$_2$]$_0$ and [RH]$_0$ are the initial concentrations of alkyl nitrates and the parent hydrocarbons before photochemical processing, respectively, $\text{[OH]}$ is the
diurnal average concentration of the OH radical. The relationships of alkyl nitrates
with their parent hydrocarbons derived from the preceding equation are comparatively
independent of the variations of OH and photolysis rates of alkyl nitrates (Roberts et
al., 1998; Wang et al., 2013). If the initial concentrations of alkyl nitrates and RH are
zero, Equation 1 can be expressed as follows (Equation 2):

\[ \frac{RONO_2}{RH} = \frac{\beta k_A}{k_B - k_A} (1 - e^{(k_A - k_B)t}) \quad (\text{Equation 2}) \]

The relationships between alkyl nitrates and RH are obtained by plotting the
measured ratios of RONO₂/RH to a specific ratio, 2-BuONO₂/n-butane. The
2-BuONO₂/n-butane ratio has been widely used in the analysis of alkyl nitrates because
n-butane is typically one of the most abundant hydrocarbons and 2-BuONO₂ is the
dominant alkyl nitrate (Roberts et al., 1998; Wang et al., 2013; Worton et al., 2010).
Although some studies have investigated the relationships between alkyl nitrates and
their parent hydrocarbons using zero initial values of alkyl nitrates, more recent
studies have used non-zero initial values of alkyl nitrates to evaluate the influence of
background levels on the photochemical evolution of alkyl nitrates (Reeves et al.,
2007; Russo et al., 2010; Wang et al., 2013). Therefore, in addition to zero initial
ratios, non-zero initial ratios of RONO₂/RH, equal to the lowest values from 0000 to
0700 measured at TMS and TW, respectively, as suggested by Wang et al. (2013),
were used to investigate the relationships between alkyl nitrates and their parent
hydrocarbons in this study. The diurnal average OH mixing ratios were simulated
using the PBM-MCM (Lyu et al., 2016). By providing the values of photochemical
processing time (t), the predicted ratios of RONO₂/RH were calculated since other
parameters, i.e., k₂, k_B, α₁, α₂ and J_RONO₂ were obtained from literature (Clemitshaw et
al., 1997; Simpson et al., 2003; Worton et al., 2010; Wang et al., 2013). In this study,
the given photochemical processing time ranged from 30 min to 2 days. The curves
generated with zero initial values were the pure photochemical (PP) curves for the
evolution of alkyl nitrates, and the curves with non-zero values, defined as
background initial ratio (BIR) curves, were generated by assuming that both
photochemical formation and background levels contributed to the distribution of
alkyl nitrates (Russo et al., 2010; Wang et al., 2013). Consistent with previous studies (Russo et al., 2010; Wang et al., 2013), the shapes of the BIR curves were different from those of PP curves. The BIR curves of C$_1$-C$_3$ alkyl nitrates at both sites were positioned above their PP curves at shorter processing time ($t < 1$ d) and converged towards the PP curves at longer processing times ($t = 1.5$-$2$ d) (Figure 5), resulting from the decreased influence of the parameter $rac{[\text{RONO}_2]_0}{[\text{RH}]_0} e^{(t-k_B \Delta e)}$ on the difference between the two curves as the photochemical age increased (Wang et al., 2013). This feature was more pronounced for C$_3$-C$_4$ alkyl nitrates at TW (Figure 6) because of the lower values of $[\text{RONO}_2]_0/[\text{RH}]_0$ resulting from the high mixing ratios of propane and $n$-butane (Ling and Guo, 2014). Figure 5 presents the relationships of C$_1$-C$_3$ RONO$_2$/RH to 2-BuONO$_2$/n-butane at TMS. The red dashed curves are pure photochemical curves, while the blue solid curves are BIR curves with the lowest ratios of RONO$_2$/RH from 0000 to 0700 LT as the background initial ratio. Similarly, Figure 6 shows the relationships of C$_1$-C$_3$ RONO$_2$/RH to 2-BuONO$_2$/n-butane at TW.

Figure 5. Relationships of C$_1$-C$_3$ RONO$_2$/RH with 2-BuONO$_2$/n-butane at TMS. The red dashed curves were obtained based on zero initial concentrations of RH and alkyl nitrates (pure photochemical curves, PP), while the blue solid curves were obtained based on non-zero initial levels (background initial ratio curves, BIR), with the lowest ratios of RONO$_2$/RH from 0000 to 0700 LT.
Figure 6. Relationships of $C_1$-$C_3$ RONO$_2$/RH with 2-BuONO$_2$/n-butane at TW. The red dashed curves were obtained based on zero initial concentrations of RH and alkyl nitrates (pure photochemical curves, PP), while the blue solid curves were obtained based on non-zero initial levels (background initial ratio curves, BIR), with the lowest ratios of RONO$_2$/RH from 0000 to 0700 LT.

At TMS, the measured ratios of MeONO$_2$/methane and EtONO$_2$/ethane to 2-BuONO$_2$/n-butane were much higher than the ratios in the PP curves (Figure 5c & d), with the observed ratios larger than their theoretical ratios by factors of 5-25. As expected, the observed trends approached the PP curves at a longer processing time, suggesting that the measured ratios of $C_1$-$C_2$ RONO$_2$/RH to 2-BuONO$_2$/n-butane were influenced by aged air masses resulting from their relatively long atmospheric lifetimes and the slow photochemical reaction rates of methane and ethane (Worton et al., 2010; Russo et al., 2010). However, the difference between the measured ratios and the predicted ratios of $C_1$-$C_2$ RONO$_2$/RH to 2-BuONO$_2$/n-butane in BIR curves was comparatively smaller, further confirming that there were other sources contributing to ambient $C_1$-$C_2$ alkyl nitrates besides photochemical formation, including the background levels of $C_1$-$C_2$ alkyl nitrates and their parent hydrocarbons (direct measurements of RH in Table 1) (Wang et al., 2013). For example, the average
MeONO$_2$ and EtONO$_2$ mixing ratios at Hok Tsui, a PRD regional background site, were 10.4 ± 0.7 and 9.6 ± 0.7 pptv (unpublished data, 2001-2002), respectively. Regarding the C$_3$ alkyl nitrates, the measured ratios of 1- and 2-PrONO$_2$/propane to 2-BuONO$_2$/n-butane were closer to the ratios of the BIR curve than those of the PP curve at TMS, further indicating the influence of background C$_3$ alkyl nitrates and their parent hydrocarbons. However, the evolution of the measured ratios of C$_3$ RONO$_2$/RH to 2-BuONO$_2$/n-butane agreed well with the predicted ratios of BIR and PP curves at TMS, indicating that secondary formation from propane oxidation contributed significantly to the ambient C$_3$ alkyl nitrates, including the background C$_3$ alkyl nitrates. Consistent with previous studies, the slopes of the observed ratios of C$_3$ RONO$_2$/RH to 2-BuONO$_2$/n-butane were different from those in the PP and BIR curves (Russo et al., 2010; Wang et al., 2013). For example, the slopes of the observed ratios of 1- and 2-PrONO$_2$/propane to 2-BuONO$_2$/n-butane were 0.04 ± 0.01 and 0.26 ± 0.02, respectively, while the slopes for the BIR curves were 0.02 ± 0.01 (PP curve: 0.02 ± 0.01) and 0.12 ± 0.01 (0.10 ± 0.01), respectively. This was reasonable as the difference in the number of samples and distribution of data between the observed ratios and the ratios of PP and BIR curves, particularly when the observed ratios were higher than the theoretical ones because of significant influence of the background levels of alkyl nitrates and RH (Russo et al., 2010; Wang et al., 2013). Therefore, to further investigate the influence of secondary formation and background mixing ratios on C$_3$ alkyl nitrates at TMS, the ratio of 1-/2-PrONO$_2$ was examined. Previous studies reported that the theoretical ratio of 1-/2-PrONO$_2$ was the ratio between the yield for 1-PrONO$_2$ and 2-PrONO$_2$ formation, which was equal to the ratio of $\beta_{1-PrONO_2}/\beta_{2-PrONO_2}$ (0.21) (Simpson et al., 2003; Wang et al., 2013). If photochemical production was the dominant source of 1-PrONO$_2$ and 2-PrONO$_2$, the observed ratios should be close to the theoretical ones. Indeed, the slope of 1-PrONO$_2$ and 2-PrONO$_2$ at TMS was 0.19 ($R^2 = 0.86, p < 0.05$), close to the theoretical ratio (0.21), confirming that photochemical production from propane, including in-situ photochemical production and transport of photochemically-formed C$_3$ alkyl nitrates in urban areas and/or during transit from urban areas to TMS, was the dominant source of ambient
C₃ alkyl nitrates.

At TW, the comparison between the observed ratios of C₁-C₂ RONO₂/RH to 2-BuONO₂/n-butane and the ratios from the PP and BIR curves was consistent with that at TMS. However, in terms of C₃ alkyl nitrates, although the evolution of the measured ratios of C₃ RONO₂/RH to 2-BuONO₂/n-butane followed the trends of the ratios in the PP and BIR curves, the measured ratios of C₃ RONO₂/RH to 2-BuONO₂/n-butane at TW were further away from the PP/BIR curves, about 2-3 times the ratios in the PP and BIR curves, implying additional sources of C₃ alkyl nitrates (Wang et al., 2013) (details in Section 3.2.2). High emissions of propane provided sufficient precursors of C₃ alkyl nitrates, and the lifetimes of 1-PrONO₂ and 2-PrONO₂ were long enough to sustain relatively high levels at TW. To further investigate the influence of additional sources on the distributions of C₃ alkyl nitrates at TW, equation 1 was used to fit the measured ratios of 1- and 2-PrONO₂/propane to calculate the yield of C₃ alkyl nitrates (β). The average yields of 1- and 2-PrONO₂ were 0.032 ± 0.004 and 0.22 ± 0.02, respectively, higher than the laboratory kinetic values by factors of 4—9 (Kwok and Atkinson, 1995). This confirms the presence of additional emissions of C₃ alkyl nitrates at TW, including locally-emitted C₃ alkyl nitrates and/or secondary formation other than the production pathway from propane to proxyl radical and PrONO₂ (Reeves et al., 2007; Worton et al., 2010). The slope of 1-PrONO₂ to 2-PrONO₂ at TW was 0.15 (R² = 0.80, p < 0.05), lower than the theoretical ratio of 0.21, further demonstrating the influence of other significant sources on ambient mixing ratios of C₃ alkyl nitrates at TW.

3.2.2. Source apportionment of alkyl nitrates

Figure 7 presents the explained variations of species (as a percentage of the species total) in the identified sources extracted by the PMF model. The standard error in Figure 7 was obtained from a bootstrap analysis of the PMF model simulation. The source profiles of the alkyl nitrates and their parent hydrocarbons were altered resulting from photochemical transformation during transport to the TMS site. Therefore, only the data collected at the urban site were used for source apportionments of alkyl nitrates.
High concentrations of O$_x$ and alkyl nitrates were found in the first factor at both sites, implying that this factor was associated with secondary formation. In addition, certain amounts of combustion species, such as ethane, ethyne, propane, $i/n$-butanes, benzene and CO were present in this factor. It is not surprising that O$_x$ correlated with the aforementioned species given that O$_3$ is a secondary pollutant formed from photochemical oxidation of RH (Ling and Guo, 2014). The second factor was distinguished by a significant presence of methyl chloride, ethene, ethyne and benzene along with certain amounts of methane, propane and $i/n$-butane. It is well established that methyl chloride, ethyne and benzene are typical tracers for biomass burning/biofuel combustion (Barletta et al., 2009; Guo et al., 2011). As biofuel was not in widespread use in Hong Kong (HKCSD, 2010), this factor was identified as biomass burning. The third factor was identified as oceanic emissions, as the tracer DMS had an exclusively high percentage in this source at both sites (Blake et al., 2003; Marandino et al., 2013). The last factor was dominated by high percentages of propane and $i/n$-butanes, typical tracers of liquefied petroleum gas (LPG). Therefore, this factor was identified as LPG usage.

![Explained variations of species in the identified sources extracted by the PMF model for TW.](image)

As mentioned earlier, regional transport and mesoscale circulation had a significant influence on the distribution of air pollutants at TMS and TW (Guo et al., 2012, 2013a). By using the Weather Research and Forecasting (WRF) model, air...
masses affected by mesoscale circulation were distinguished from those affected by regional transport (Guo et al., 2013a). Nine sampling days during the entire sampling period (24, 29-31 October, 1-3, 9 and 19 November) were identified to be affected by mountain-valley breezes (they were also O₃ episode days). Hence, we divided the sampling period into two categories - “meso” and “non-meso” scenarios for source apportionment analysis. The “meso” scenario included the nine O₃ episode days with apparent mesoscale circulation, while the “non-meso” scenario covered the rest of the sampling days.

By summing up the mass of the alkyl nitrates in each source category, the overall mixing ratios in each source were obtained and the contribution of each individual source to alkyl nitrates at both sites was calculated. Figures 8 and 9 present the source contributions to individual alkyl nitrates for the “meso” and “non-meso” scenarios in percentage and in mixing ratio at TW, respectively. The mixing ratios of total alkyl nitrates (\( \sum \text{RONO}_2 = \text{MeONO}_2 + \text{EtONO}_2 + \text{1-PrONO}_2 + \text{2-PrONO}_2 + \text{2-BuONO}_2 \)) were higher in the “meso” scenario than those in “non-meso” scenario (\( p < 0.05 \)), with the average value of 100.9 ± 7.5 pptv for total alkyl nitrates in the “meso” scenario, about 1.4 times those in the “non-meso” scenario. It was found that in the “meso” scenario, secondary formation was the most significant contributor to the total alkyl nitrates mixing ratios, with an average percentage of 60 ± 2% or absolute mixing ratio of 60.2 ± 1.2 pptv, followed by biomass burning (34 ± 1% or 35.1 ± 0.4 pptv) and oceanic emissions (6 ± 1% or 5.62 ± 0.06 pptv). For the “non-meso” scenario, the contributions of biomass burning (46 ± 2% or 34.2 ± 0.7 pptv) and secondary formation (44 ± 2% or 32.9 ± 0.7 pptv) were comparable, and the oceanic emissions contributed 10 ± 1% or 7.0 ± 0.07 pptv to the total alkyl nitrates. The higher contribution of secondary formation in the “meso” scenario at TW was mainly associated with higher degree of photochemical reactions. Indeed, the PBM-MCM model simulation indicated that the average concentration of HOₓ (HOₓ = OH + HO₂) during daytime hours (0700-1800 LT) in the “meso” scenario was \((2.5 ± 0.7) \times 10^7\) molecule/cm³, about twice that of the “non-meso” scenario.
Figure 8. Source contributions to individual alkyl nitrates in (a) “meso” and (b) “non-meso” scenarios at TW (in percentage).

Figure 9. Source contributions to individual alkyl nitrates in (a) “meso” and (b) “non-meso” scenarios at TW (in summed mixing ratio).

In addition, although the percentage contribution of biomass burning was higher in the “non-meso” scenario, the absolute mixing ratios of biomass burning were comparable in the two scenarios. Figure 10 shows the diurnal patterns of $\Sigma$ RONO$_2$ from biomass burning and oceanic emissions in “meso” and “non-meso” scenarios at TW. The contribution of biomass burning in the “meso” scenario was likely attributable to local emissions, including the cooking/heating activities in the small villages nearby and the frequent barbecue activities at the base of the mountain (Guo et al., 2013a, b), as well as the forest fires observed in the mountainous areas (AFCD, 2015). The regular cooking/heating activities from 0700 to 1400 LT in many dim sum restaurants in the village likely resulted in the increased levels of biomass burning in the morning until noon. In contrast, the diurnal pattern in “non-meso” scenario was weak and the maximum values were not statistically different from the minimum values. The difference of the average mixing ratio of $\Sigma$ RONO$_2$ between daytime and nighttime hours was only 1 pptv for biomass burning. The weak diurnal variations in
the “non-meso” scenario suggests that the contribution of fresh biomass burning emissions was insignificant, revealing the influence of regional transport from the PRD region. This speculation was confirmed by the analysis of 12-h backward trajectories, which showed that air masses in the “non-meso” scenario were mainly from the inland PRD region (not shown). It is noteworthy that although air masses were more aged in the “non-meso” scenario, the levels of alkyl nitrates were comparable to those in the “meso” scenario, highlighting the strong emissions of biomass burning in the PRD region (Yuan et al., 2010).

For the oceanic emissions, a minimum mixing ratio during daytime hours was found for $\Sigma$ RONO$_2$ in the “meso” scenario, while a broad peak was present during daytime hours in the “non-meso” scenario. The daytime minimum mixing ratio in the “meso” scenario at TW was related to uplifted valley breezes that brought alkyl nitrates away from TW to TMS, while the higher nighttime values were probably owing to marine emissions and aged continental plumes which were re-circulated from the South China Sea to the coastal urban site at night. In contrast, the broad daytime peak in the “non-meso” scenario was likely associated with higher daytime temperature and solar radiation, leading to higher oceanic emissions that were transported from eastern China and southern China coastal regions to the TW site.

![Figure 10](image.png)

Figure 10. Diurnal patterns of (a) biomass burning and (b) oceanic emissions for “meso” and “non-meso” scenarios at TW.

Moreover, the contributions of oceanic emissions to C$_1$-C$_2$ alkyl nitrates were higher than C$_3$-C$_4$ alkyl nitrates, with average percentages of 23% and 32% for the “meso” and “non-meso” scenarios (Figures 8 and 9), suggesting the importance of oceanic emissions to C$_1$-C$_2$ alkyl nitrates, consistent with the results of previous work.
The C₃-C₄ alkyl nitrates were dominated by the secondary formation in the “meso” scenario (58-71%), while the contributions of biomass burning and secondary formation to C₃-C₄ alkyl nitrates were comparable in the “non-meso” scenario.

3.2.3. Contributions of mesoscale circulation, in-situ formation and regional transport to alkyl nitrates at TMS

Valley breezes transported freshly-emitted parent hydrocarbons and alkyl nitrates from the urban areas at the base of the mountain (TW) to the mountain summit (TMS) during daytime hours, redistributing the ambient levels of alkyl nitrates at TMS (Guo et al., 2013a; Lam et al., 2013). Except for MeONO₂, which had comparable levels in both “meso” and “non-meso” scenarios, the mixing ratios of daytime C₂-C₄ alkyl nitrates were all higher in “meso” scenario than those in “non-meso” scenario (p < 0.05), with the average values of 14.21±0.79, 28.73±1.70, 4.67±0.29 and 40.21±2.79 pptv for EtONO₂, i-PrONO₂, n-PrONO₂ and 2-BuONO₂, respectively. To quantify the influence of mesoscale circulation on the mixing ratios of alkyl nitrates at TMS, a moving box model coupled with master chemical mechanism (Mbox) was applied to the data collected on the days influenced by mesoscale circulation (i.e., “meso” scenario) (Guo et al., 2013a). The model was developed based on an idealized trajectory movement between TMS and TW sites, with air pollutants transported from TW to TMS through the valley breeze during daytime hours (0800-1700 LT) when photochemical formation of alkyl nitrates was occurring, contributing to their ambient levels at TMS. As such, the model was only constrained with the observed daytime data at TW. On the other hand, the night-time downslope flow occurred because of the mountain breeze after sunset until the next morning, and TMS was set as the center of the box model, which was constrained by the data collected at TMS only for that period (Lam et al., 2013).

Table 3 presents the average concentrations of C₁-C₄ alkyl nitrates simulated by the Mbox model at TMS, i.e., the values under the “meso” scenario. It should be noted that the comparison was only made for daytime alkyl nitrates (0800-1700LT), when the valley breeze occurred. The average mixing ratios of MeONO₂, EtONO₂,
1-PrONO$_2$, 2-PrONO$_2$ and 2-ButONO$_2$ at daytime hours estimated using the Mbox model were 9.97 ± 0.85, 7.38 ± 0.44, 3.08 ± 0.16, 18.7 ± 0.77 and 34.7 ± 3.14 pptv, respectively, accounting for 86%, 52%, 66%, 65% and 86% of the observed values at TMS during the same period, respectively. These results demonstrate that when there was mesoscale circulation, the alkyl nitrate levels at TMS were dominated by the photo-oxidation of their parent hydrocarbons that originated from the urban site TW. Although the mixing ratios of the parent hydrocarbons were lower at TMS, this is still one possible explanation leading to the similar levels of alkyl nitrites measured at the two sites.

For the “non-meso” scenario, the simulated levels of in-situ formation of MeONO$_2$, EtONO$_2$, 1-PrONO$_2$, 2-PrONO$_2$ and 2-BuONO$_2$ at TMS were 3.61 ± 0.48, 2.18 ± 0.29, 1.03 ± 0.13, 3.68 ± 0.45 and 10.9 ± 1.31 pptv, respectively, accounting for 18-42% of the observed C$_1$-C$_4$ alkyl nitrates, indicating that other sources rather than local photochemical formation made significant contributions to ambient levels of alkyl nitrates. As stated earlier, TMS was a mountain site with sparse anthropogenic emissions nearby. However, the prevailing synoptic northerly winds in “non-meso” scenario suggested possible regional sources of alkyl nitrates from inland PRD region to the mountain site. The impact of regional transport on the variations of air pollutants at TMS for the days without mesoscale circulation, especially when the prevailing winds were from the north with high speeds, was corroborated in Guo et al. (2013a). By excluding the locally-formed alkyl nitrates from their overall levels, the contribution of regional sources to alkyl nitrates was determined for TMS. The regional source contributions to MeONO$_2$, EtONO$_2$, 1-PrONO$_2$, 2-PrONO$_2$ and 2-BuONO$_2$ were 7.07 ± 0.50, 8.44 ± 0.62, 2.11 ± 0.22, 16.86 ± 1.17, and 15.15 ± 1.49 pptv, respectively, accounting for 58-82% of the alkyl nitrates measured at TMS. It is noteworthy that the regional alkyl nitrates included influences from all source categories (photochemical formation, biomass burning and oceanic emissions) for the inland PRD region.
Table 3. Mixing ratios of C1-C4 alkyl nitrates influenced by mesoscale circulation (“Meso”), in-situ formation and regional transport at TMS (unit: pptv).

<table>
<thead>
<tr>
<th>Scenario</th>
<th>MeONO2</th>
<th>EtONO2</th>
<th>1-PrONO2</th>
<th>2-PrONO2</th>
<th>2-BuONO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>“Meso”</td>
<td>9.97 ± 0.85</td>
<td>7.38 ± 0.44</td>
<td>3.08 ± 0.16</td>
<td>18.7 ± 0.77</td>
<td>34.7 ± 3.14</td>
</tr>
<tr>
<td>In-situ formation</td>
<td>3.61 ± 0.48</td>
<td>2.18 ± 0.29</td>
<td>1.03 ± 0.13</td>
<td>3.68 ± 0.45</td>
<td>10.9 ± 1.31</td>
</tr>
<tr>
<td>Regional transport</td>
<td>7.07 ± 0.50</td>
<td>8.44 ± 0.62</td>
<td>2.11 ± 0.22</td>
<td>16.86 ± 1.17</td>
<td>15.15 ± 1.49</td>
</tr>
</tbody>
</table>

3.3. Relationship of alkyl nitrates with O3

Alkyl nitrates are mainly formed through the reaction of peroxy radical (RO2) and NO. However, NO can be oxidized by RO2 to form NO2, which results in tropospheric O3 formation through NO2 photolysis. Hence, investigating the relationship between alkyl nitrates and O3 is useful for evaluating the influence of alkyl nitrates on O3 formation (Simpson et al., 2006). Since photochemical formation of O3 and alkyl nitrates occurs during daytime hours, the relationship between O3 and alkyl nitrates is usually evaluated using the observed daytime data (i.e., 0900-1600 LT). In this study, the “oxidant” OX (O3 + NO2) was considered to be a better representation of O3 levels as it takes into account the effect of O3 titration by NO.

Figure 11 shows the correlation between OX and the total alkyl nitrates (ΣRONO2) at daytime hours. Good correlations were found at TMS (R² = 0.63) and TW (R² = 0.56) with the slopes of 0.67 and 0.47 ppbv/pptv, respectively, suggesting that when 1 pptv of total alkyl nitrates were formed from the reaction of RO2 and NO, 0.67 and 0.47 ppbv of OX could be simultaneously produced at TMS and TW, respectively. The relatively higher slope at TMS than at TW was owing to higher concentrations of HOX radicals and higher photochemical reactivity of VOCs at TMS (Lyu et al., 2016).

Additionally, as the formation of alkyl nitrates consumes NO, this process results in a negative contribution to O3 formation. To quantify the negative influence on O3, the PBM-MCM model was applied to the whole data collected at TMS and TW, respectively (Lyu et al., 2016). The formation of alkyl nitrates made negative contributions to the O3 production, with the average reduction of 64.6 (TW: 24.9), 37.4 (11.0), 18.9 (2.6), 39.6 (11.1), and 115.1 (40.6) pptv of O3 for the formation of
MeONO₂, EtONO₂, 1-PrONO₂, 2-PrONO₂ and 2-BuONO₂ at TMS, respectively. Furthermore, moderate to good correlation was found between the simulated O₃ reduction and the photochemically formed alkyl nitrates at TMS (R² = 0.42) and TW (R² = 0.72), with the average O₃ reduction rate of 4.1 and 4.7 pptv/pptv, respectively. Namely, O₃ was reduced by 4.1 and 4.7 pptv if 1 pptv of alkyl nitrates were formed at TMS and TW, respectively.

Moreover, because secondary alkyl nitrates are formed through two main reaction pathways, “RO₂ + NO” and “RO + NO₂”, it is of interest to investigate the relative contribution of the above pathways to the formation of alkyl nitrates. Two scenarios for model simulations were run and compared. The first scenario was the base case in which the model was run with all reaction pathways opened, while the second scenario was the constrained case in which the pathway of RO₂ + NO → RONO₂ was shut down. It was found that the reaction of “RO₂ + NO” was the prominent pathway for the secondary formation of alkyl nitrates at the two sites. The contributions of CH₃O₂ + NO to MeONO₂ accounted for about 72% and 50% of the secondarily formed MeONO₂, while the contributions of RO₂ + NO were 97-99 and 95-99% of the secondarily formed C₂-C₄ alkyl nitrates at TMS and TW, respectively. These results are similar to the findings obtained at Tai O, Hong Kong (Lyu et al., 2015). The lower contributions of RO₂ + NO to MeONO₂ at the two sites were related to the higher levels of CH₃O from the oxidation of CH₄ and the decomposition of larger RO₂ radicals.
4. Conclusions

Intensive field measurements of alkyl nitrates and their parent hydrocarbons were conducted concurrently at a mountain site (TMS) and an urban site (TW) at the base of the same mountain in Hong Kong from September to November 2010. The levels of MeONO$_2$, EtONO$_2$ and 2-PrONO$_2$ were slightly higher at TW than at TMS ($p < 0.05$), while the average mixing ratios of 1-PrONO$_2$ and 2-BuONO$_2$ were comparable at the two sites ($p > 0.05$). However, the levels of the parent hydrocarbons of alkyl nitrates were lower at TMS, implying the complexity of sources of alkyl nitrates. Receptor model and photochemical box model simulations found that mesoscale circulation and regional transport had a significant impact on the levels of alkyl nitrates at the two sites. At TW, secondary formation was the dominant contributor to alkyl nitrates when there was mesoscale circulation, while the contributions of secondary formation and biomass burning were comparable under the influence of regional transport. At TMS, photo-oxidation of the parent hydrocarbons from TW contributed 52-85% to the ambient levels of alkyl nitrates on the days with mesoscale circulations between the two sites. On the other hand, alkyl nitrates from the inland PRD region were responsible for 58-82% of the observed values at TMS on the days with regional influence. The photo-oxidation of parent hydrocarbons from TW and regional transport resulted in similar values of alkyl nitrates observed at the two sites. With regard to the secondarily formed alkyl nitrates, the reaction of RO$_2$ and NO was the prominent pathway at both sites. Moreover, the formation of alkyl nitrates made negative contributions to the O$_3$ formation, with a reduction rate of 4.1 and 4.7 pptv O$_3$ per pptv alkyl nitrates at TMS and TW, respectively. The findings of this study will aid in understanding the source contributions and photochemical formation pathways of alkyl nitrates in Hong Kong’s mountainous areas.

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