Interactive comment on “New insight into the spatiotemporal variability and source apportionments of C1–C4 alkyl nitrates in Hong Kong” by Z. H. Ling et al.

Anonymous Referee #1

Alkyl nitrates and its formation processes are very important for the understanding of atmospheric photochemistry. However, so far there are limit number of studies investigating this issue. This study presents valuable measurement data of alkyl nitrates concurrently obtained from a mountain site and an urban site on the foot of the mountain in Hong Kong. Overall, the manuscript is well-written and is worth to be published in ACP. Before that, some minor points should be appropriately addressed.

Reply: We thank the reviewer for his/her comments. Our responses to the reviewer are as follows, along with indications of how the manuscript has been further revised for the consideration by ACP. We hope that these changes will further strengthen the main points and make them clearer in the revised manuscript.

1) The information for the sampling at Tai O should be added in the map in Figure 1 and the introduction of data, because the results at the station were used to compare with alkyl nitrates at the two stations.

Reply: The reviewer’s comment is highly appreciated. In the revised manuscript, the information for the sampling and the introduction of data at Tai O were added accordingly as follows:

“The Tai O sampling station was a rural/costal site located on the western coast of Lantau Island in southwestern Hong Kong (elevation, 80 m a.s.l.) (Figure 1). Further to the east are the urban areas, with a straight distance of 32 km, and to the northeast, north and northwest is the polluted PRD region. The Asian monsoon has a significant influence on the seasonal variations of air pollutants at Tai O. In autumn and winter, prevailing northerly winds bring anthropogenic emissions from the PRD region to Tai O, which superimpose with emissions from local urban areas. In summer, clean oceanic air masses dilute the levels of air pollutants because of the influence of dominant southerly winds. A detailed description of the site is provided in Wang et al. (2003).”

and,

“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).”

For details, please refer to Figure 1, Lines 11-20, page 6 and lines 22-29, page 7 in the
2) The authors described meteorological conditions for separated periods in Table 2. These introductions were partly repeated in the main text, but there is a lack of weather charts to support these descriptions. I would like to suggest giving figures to show representative weather chart for each period but give the Table 2 in supplementary if the authors think the table is important.

Reply: The table and the representative weather charts for each period in the table were placed in the supplementary information as Table S2 and Figure S1.

3) In the first paragraph of section 3.2.1, the authors used the method of Bertman et al. (1995), which follows three assumptions. It should be discussed whether the both stations met the assumption. For example, if TMS is a NOx-rich environment? Otherwise, the uncertainty should be discussed.

Reply: Thanks for the excellent suggestion. We have added the following into the manuscript to discuss whether the two sites met the assumption:

“As photochemical oxidation of parent hydrocarbons is an important source of alkyl nitrates, it is of help 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 NOx-rich, making the reaction with NO being the dominant pathway for the destruction of RO2 radicals (Russo et al., 2010). In this study, the average mixing ratios of NOx at TMS and TW were 10.7 ± 0.3 and 56.3 ± 1.6 ppbv, respectively, indicating that the environment was NOx-rich (> 0.1 ppbv, Roberts et al., 1998). Hence, reaction with NO was the main pathway for the destruction of RO2 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).”

For details, please refer to lines 5-20, page 16 in the revised manuscript.

4) Page 22608, at the end of first paragraph of section “Diurnal variation”, “…relatively higher levels of MeONO2 and EtONO2 were observed from midnight to early morning, which could be associated with marine air masses originating from the South China Sea as the southerly winds prevailed”. Here the southerly winds are generally associated with the delayed sea-breezes, which could bring the daytime photochemically aged pollution from land and re-circulated to the coastal region at night (Ding et al., 2004). So this pollution is only contain marine source but also aged
plumes.

**Reply:** Thanks for pointing this out. The text has been revised as follows:

“At TW, however, besides the peak concentrations observed in the afternoon, high levels of MeONO$_2$ and EtONO$_2$ 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 MeONO$_2$ and EtONO$_2$ might be 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 MeONO$_2$ and EtONO$_2$ levels from midnight to early morning on the above sampling days were related to oceanic emissions (see Section 3.2.2 for details).”

For details, please refer to lines 19-28, page 14 in the revised manuscript.

5) **Figure 4**, it will be better to show the diurnal variation of other species, such as O$_3$, NO$_y$ and the parent hydrocarbons, together with RONO$_2$.

**Reply:** Thanks for the suggestion. According to both reviewers’ comments, the discussion on the diurnal variations of air pollutants was deleted in the revised manuscript. Instead, only day-to-day variations of alkyl nitrates and their parent hydrocarbons were characterized.

For details, please refer to Section 3.1 in the revised manuscript.

6) For the alkyl nitrates measurements, Wang et al. (2003) presented results at Hok Tsui site measured during Trace-P period. Please also make some comparisons in the Figure 2 and the text.

**Reply:** Thanks for the comment. The comparison of the results at Hok Tsui with those in the present study was added in Figure 2 and the text. However, as suggested by reviewer #2, the above comparison may be biased due to the fact that the sampling conditions and sampling periods in the present study were different from those at Hok Tsui, where daily samples were taken for 1-min. and the sampling time varied on different sampling days. This could also explain the difference in observed levels among the three sites. Therefore, the following text was added in the revised manuscript as follows:

“In comparison with other studies, the average mixing ratios of alkyl nitrates at TMS........... 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.”

For details, please refer to Figure 2, and lines 14-30, page 11 and line 1, page 12 in the revised manuscript.
Interactive comment on “New insight into the spatiotemporal variability and source apportionments of C1-C4 alkyl nitrates in Hong Kong” by Z.H. Ling et al.
Anonymous Referee #2

General Comments:
1. The manuscript by Ling et al. presents alkyl nitrate and parent hydrocarbon measurements from two sites in Hong Kong; a low-elevation urban site and a high-elevation mountain site. The analysis presented in this manuscript is similar to previous studies and there is very little originality or depth to this piece of work. While the title of the manuscript poses that there are “new” insights in the spatiotemporal and source apportionments of C1-C4 alkyl nitrates in Hong Kong, I would disagree. The authors attribute the differences in alkyl nitrate distributions between the urban and mountain site to photochemical production, hydrocarbon sources, meteorological conditions and transport patterns-I would not consider these factors to be new insight, rather simply reiterating what we already know drives air mass composition in general.

Reply: The excellent comment is greatly appreciated. When we said “new insight” in the title, we meant that the present study made significant improvement on our knowledge of alkyl nitrates in Hong Kong, compared to previous studies conducted in the same city. In the past decade, only one study was conducted in Hong Kong by the same group to investigate the characteristics of alkyl nitrates based on the samples collected at a coastal site from 24 August 2001 to 31 December 2002 (Simpson et al., 2006). The seasonal and diurnal patterns of alkyl nitrates were studied. The high MeONO2 levels during the pollution episodes were assumed to be related to the reaction of methoxy radical (CH3O) with NO2, which needed confirmation from further measurements and modeling. We do appreciate the previous study, which provided a first insight into the abundance and temporal variations of alkyl nitrates and their impact factors in Hong Kong. By comparison, we have improved the following aspects in the present study: 1) the sampling methods. In the previous study, each whole-air sample at Tai O was collected for only 1-min. Except for the intensive sampling conducted from 0700-1900 LT every 2-hours on the selected 15 pollution episode days, most of the samples were taken daily or every few days. Also, though the samples were mainly collected in the midafternoon, the sampling time on each sampling day was different. In contrast, in this study, intensive field measurements were conducted simultaneously at two sites on 10 non-O3 episode days and 10 O3
The sampling duration for each sample was 1 hour. During non-O$_3$ episode days, each whole air sample was collected every 2-hours from 0700-1900 LT, while on O$_3$ episode days, integrated 1-hour sample was collected every hour from 0900-1600 LT, with additional samples collected at 0000, 0300 and 0700 LT. The sampling design and methods in the present study were more precise and more appropriate for the investigation of the variations of alkyl nitrates and their parent hydrocarbons and their relationships, and for model simulation of source apportionments and related photochemical reactivity of alkyl nitrates and their hydrocarbons in Hong Kong. 2) The importance of data. Due to rapid economic development and stricter regulations of vehicular emissions and solvent usage in the past 15 years, the ambient composition and emission sources of VOCs have remarkably changed in Hong Kong. It is expected that this study would provide “new insight” into the alkyl nitrates. 3) The data analysis. The previous study by Simpson et al. (2006) solely relied on the analysis of measurement data, while in this study, we for the first time quantified the source apportionments of alkyl nitrates and investigated relationship of alkyl nitrates with their parent hydrocarbons for Hong Kong. This was achieved with the aid of receptor model and photochemical box model incorporating explicit Master Chemical Mechanism (MCM), developed by our own team. In particular, the impact of mesoscale circulation, regional transport and photo-oxidation on the redistribution of alkyl nitrates was quantified. Moreover, the relationship between alkyl nitrates and O$_3$ production, and the dominant reaction pathways of the secondary formation of alkyl nitrates were for the first time determined and quantified in this study.

We appreciate that the methodologies used in this study, such as a simplified sequential reaction model for the relationship of alkyl nitrates with their parent hydrocarbons, and the PMF model for source apportionments, were already used in previous studies (e.g., Russo et al., 2010; Worton et al., 2010; Wang et al., 2013). However, this study made significant progress on quantitative estimation of the source contributions of alkyl nitrates in Hong Kong, compared to the previous study. In particular, this study for the first time used a self-developed PBM-MCM to quantify
the contributions of mesoscale circulation and regional transport to the levels of alkyl nitrates, the roles of alkyl nitrates in O₃ formation, and the contributions of different reaction pathways to alkyl nitrate formation in Hong Kong. Hence, we used “new insights” in the title.

2. There are no major conclusions drawn from the results of this work. Moreover, there is a flawed assessment made regarding the photochemical age using the pure photochemical age using the pure photochemical alkyl nitrate evolution curves when comparing them to the measurements-this will be addressed in the specific comments section. In terms of language, there is an overuse of “i.e.” (I think I counted 25 of them, and most were not needed) and “due to” in addition to the inappropriate wording/word choices throughout the document (e.g., “...the weather turned fine...”). Also, it would be beneficial to the reader if figures 3-6 were improved-it is difficult to differentiate between the sites, particularly for 5 and 6-there are additional details regarding figures 5 and 6 that will be addressed in the specific comments section.

Reply: Thanks for the valuable comments. Accordingly, the manuscript has been significantly revised and reorganized. The revised version focused on the abundance and source apportionments of alkyl nitrates, the contributions of mesoscale circulations and regional transport, the relationship of alkyl nitrates with the O₃ formation, and the contributions of different reaction pathways to secondarily-formed alkyl nitrates at the two sites. The major findings were revised in the abstract as follows:

“C₁-C₄ alkyl nitrates (RONO₂) were measured concurrently at a mountain site (TMS) and an urban site (TW) at the foot 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 different elevations of the sites, suggesting different source contributions of alkyl nitrates at the two sites, which was proved by the analysis of photochemical evolution of alkyl nitrates. 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. On the other hand, alkyl nitrates at TMS were mainly due to the photo-oxidation of parent hydrocarbons at TW when mesoscale circulation, i.e., valley breezes occurred, contributing 52–86% to the levels of alkyl nitrates at TMS. In contrast, 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 (RO$_2$) with nitrous oxide (NO) dominated the formation of RONO$_2$ at both sites, and the formation of alkyl nitrates contributed negatively to O$_3$ production, with average reduction rates of -4.1 and -4.7 pptv/pptv at TMS and TW, respectively.” For details, please refer to the “Abstract” in the revised manuscript.

For the flawed assessment of the photochemical ages using the pure photochemical alkyl nitrate curves, the discussion of this assessment was deleted in the revised manuscript. For details, please refer to Section 3.2 in the revised manuscript.

For the language use, we have deleted some inappropriate use of “i.e.” and “due to”, and/or replaced others by appropriate terms. The revised manuscript has also been double-checked by native English speakers.

Lastly, all the figures in the manuscript have been revised, including the fonts, colors, legends and the resolution of the figures. The detailed revision is addressed in the “specific comments” section.

3. In its current form, I do not feel the manuscript is well organized. After several readings, I continually found myself asking the same questions at the same points throughout the paper; the discussion does not flow in a logic manner. Additionally, there needs to be a more thorough analysis of the data—what is presented is superficial and thin. In comparison to other alkyl nitrate papers, it falls short on both presentation and interpretation. While PMF was used to aid in source identification, it would have been useful to include the additional data (either in the manuscript or as supplemental information) that was used for the PMF analysis to enhance/corroborate the PMF results.

Reply: We thank the reviewer for the invaluable suggestion. As the content in the manuscript has been revised, the “Results and discussion” section has been re-organized as follows:

Section 3.1 presents the general characteristics of alkyl nitrates and their parent hydrocarbons to reveal the difference of alkyl nitrates and their parent hydrocarbons between the two sites, and to compare with other studies. In section 3.2, the relationship of alkyl nitrates with their parent hydrocarbons is qualitatively explored to investigate the influence of secondary formation and other sources on the levels of
the alkyl nitrates. The source apportionments of alkyl nitrates at TW under the “meso” and “non-meso” scenarios are then conducted using the PMF model, while the contributions of mesoscale circulation and regional transport to the alkyl nitrates at TMS are determined by a moving box model with master chemical mechanism (Mbox) and the PBM-MCM model, respectively. Lastly, in section 3.3, the correlation of alkyl nitrates with O$_3$ formation, and the contributions of different reaction pathways to the formation of alkyl nitrates are evaluated using the PBM-MCM model. The detailed description of the revisions is provided below in the responses to the following specific comments.

For the PMF model simulation, descriptive statistics of the data input in the PMF model are provided as supplemental information (Table S1).

4. Finally, the authors spend a considerable amount of time comparing their measurements to measurements made at Tai O from 2001-2002. First, the reader is given no reference to where Tai O is located and why it should be compared with the current data set – it would be useful to include pieces of information that Tai O is X km from the current sites and is located in the Pearl River Delta, etc. Next, the reader has no real frame of reference for the Tai O comparison other than it is also located in China–this should be expanded upon. Furthermore, I would not consider the measurements presented and those from Tai O to be a representative comparison, as described in the paper. The authors try to infer differences between the Tai O measurements and theirs, but the fact is that the Tai O measurements were heavily biased towards sampling ozone events, so one would expect differences between the data sets, but this isn’t appropriately addressed in the paper. Lastly, there is very little discussion about the coastal and marine influences overall and how this affects the measurements at Tai O and the Hong Kong urban and mountain sites. While there is merit in including Tai O in the analysis, the authors have not framed it well nor harvested the information from the analysis by Simpson et al. (2006) to provide any new insight in their manuscript.

**Reply:** Thanks for pointing this out. The description of the Tai O site is provided in the revised manuscript as follows:

“The Tai O sampling station was a rural/costal site located on the western coast of Lantau Island in southwestern Hong Kong (elevation, 80 m a.s.l) (Figure 1). Further to the east are the urban areas, with a straight distance of 32 km, and to the northeast, north and northwest is the polluted PRD region. The Asian monsoon has a significant influence on the seasonal variations of air pollutants at Tai O. In autumn and winter, prevailing northerly winds bring anthropogenic emissions from the PRD region to Tai O, which superimpose with emissions from local urban areas. In summer, clean
oceanic air masses dilute the levels of air pollutants because of the influence of dominant southerly winds. A detailed description of the site is provided in Wang et al. (2003).”

For details, please refer to lines 11-20, page 6 in the revised manuscript.

In addition, we agreed with the reviewers about the comparison of the results in this study with those at Tai O. As replied in the first “General comment”, the sampling methods and the sampling periods at Tai O were significantly different from those in the present study, which likely biased the comparison between the data at Tai O and those in this study. Therefore, we only compared the mixing ratios of alkyl nitrates and their parent hydrocarbons at TMS and TW with those at Tai O, while the discussion on the observed ratios of alkyl nitrates/parent hydrocarbons and the predicted ratios, and the source apportionment of alkyl nitrates at Tai O was deleted in the present study. In addition, the sampling procedures at Tai O were added in the revised manuscript as follows:

“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).”

Please refer to lines 22-29, page 7 for details.

And, the limitation for the comparison between this study and Tai O study was added as follows:

“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.”

For details, please refer to lines 24-30, page 11 and line 1, page 12 in the revised manuscript.
Lastly, Section 3.2.2 “Source apportionments of alkyl nitrates” in the revised manuscript presented some discussion about the influence of marine emissions on the alkyl nitrates at different sites. Please refer to Section 3.2.2 for details.

Specific Comments

Abstract-last sentence:
The findings of the source apportionments and photochemical evolution of RONO2 are helpful to evaluate photochemical processing in Hong Kong using RONO2 as an indicator.”
The sentence reads a bit awkwardly; how are alkyl nitrates helpful? I would suggest changing to “useful” or “potentially useful”. The sentence ends abruptly – as an indicator of what? Please revise.

Reply: Many thanks for pointing this out. Since the manuscript has been significantly revised and re-organized, the “Abstract” has been completely rewritten as replied in the second “General comment” above, in which the above sentence has been deleted.

Introduction While alkyl nitrates are defined as RONO2, using RONO2 everywhere makes the manuscript read choppy; also, it’s more appropriate to start a sentence with “Alkyl nitrates” as opposed to RONO2 – e.g., P2, L26.

Reply: We agreed with the reviewer’s suggestion. In the revised manuscript, the RONO2 used at the beginning of a sentence have all been replaced by “Alkyl nitrates”.

In addition, all the RONO2 used in the revised manuscript were also replaced by “alkyl nitrates”, except for those used in the ratios of RONO2/RH and the equations.

Methodology P5, L22: “waist of the mountain” is not a proper term – please revise.

Reply: Thanks for pointing this out. According to the reviewer’s comment, the term of “waist of the mountain” has been revised to “on the mountainside (640 m a.s.l.)”.

For detail, please refer to line 23, page 5 in the revised manuscript.


Reply: Yes. The term of “the natural territory” was revised to “the natural landscape”.

Please refer to line 24, page 5 in the revised manuscript for detailed information.
P6, L4-6: Revise the following: “In general, the solar radiation was comparable at the two sites, and the temperature was higher and the relative humidity and wind speed were lower at the TW site (Guo et al., 2013a).”
to: “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 TW (Guo et al., 2013a).”

Reply: We are grateful for the reviewer’s comment. The text has been revised accordingly as follows:
“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).”

For details, please refer to lines 1-3, page 6 in the revised manuscript.

P6, L11-14: Revise the following sentence – main point not clearly articulated:
“Based on the average wind speed and distance, the air parcel from upwind locations, i.e., the mountain foot at a local scale and/or inland PRD at a regional scale, took about 0.6–1.6 h to arrive at the TMS site (Guo et al., 2012, 2013a).”
There’s a space after the “.” in 0.6.
To something like: “Based on the average wind speed and distances(?), air masses transported from upwind locations, on both local and regional scales, took approximately 0.6–1.6 hours to arrive at the TMS site (Guo et al., 2012, 2013a).”
Local and regional scales have different distances/footprints that are impacted by topography, so it would be useful to include the actual distances in km that you are referring to for local and regional scales. Simply using qualitative markers (base of the mountain, PRD), especially if the reader is not familiar with the area (such as myself), provide no context to what extent these are for this region.

Reply: Thanks for the invaluable suggestion. According to the reviewer’s comment, the text has been revised as follows:
“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).”

For details, please refer to lines 8-10, page 6 in the revised manuscript.

P6, L16-25: “Sixty-minute integrated VOC samples…” reads awkwardly, revise to something like the following: “Whole air samples were collected on 10 O_3 episode days and 10 non-O_3 episode days using evacuated 2 L stainless steel canisters. Each of the canister samples collected was integrated over a 60-minute sampling period.”
Inappropriate wording: “subjected to laboratory analysis” – change to “the canisters were analyzed at the University of California, Irvine (UCI).”

Reply: Thanks for the suggestion. The text was revised accordingly as follows:
“Whole air samples were collected on 10 O_3 episode days and 10 non-O_3 episode days
using evacuated 2-L stainless steel canisters. Each of the collected canister samples was integrated over a 60-min sampling duration.”

The inappropriate wording of “subjected to laboratory analysis” was deleted as later in the same paragraph we mentioned that “After the campaign, the VOC samples were sent to the University of California, Irvine (UCI) for chemical analysis.”

For details, please refer to lines 1-3, page 7 and lines 12-13, page 7 in the revised manuscript.

Revise the following: “…which were forecasted based on weather parameters and meteorological data analysis, and subsequently confirmed by the observed O_3 mixing ratios.”

What are weather parameters? Why not simply say: “…which were based on weather forecasts and meteorological data analysis, and confirmed by the observed O_3 mixing ratios.”

Reply: The reviewer’s careful suggestion was greatly appreciated. The text has been revised accordingly as follows:

“…which were based on weather forecasts and meteorological data analysis, and confirmed by the observed O_3 mixing ratios.”

For details, please refer to lines 6-8, page 7 in the revised manuscript.

On P6, L24, the language needs to be more precise – you use hourly samples, making it sound as though the samples are collected each hour, but they were collected every 2 hours. I would refer to the sample as the “integrated sample”, not hourly to distinguish between the sampling interval and the sample collection time. Moreover, simply state that the non-ozone episode days were sampled at 2 hour intervals and the ozone episode days were sampled at 1 hour intervals.

Reply: Yes. The sample was the “integrated sample”, not hourly samples. Therefore, the text has been revised as follows:

“During non-O_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_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).”

For details, please refer to lines 8-12, page 7 in the revised manuscript.

P6, L27: “the VOC samples were delivered to UCI: : :” should be “the canister samples were sent to UCI…”

Reply: Thanks for the suggestion. The text was revised as follows:
“…, the canister samples were sent to University of California, Irvine (UCI) for chemical analysis.”
For details, please refer to line 13, page 7 in the revised manuscript.

P7, L5: “…the C2, C2, C2 and C2 RONO2, respectively” All of the subscripts are C2s – please correct.
Reply: Sorry for the mistake. The text was corrected as follows:
“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 C1, C2, C3 and C4 alkyl nitrates, respectively (Simpson et al., 2011).”
For details, please refer to lines 15-19, page 7 in the revised manuscript.

P7, L10-13: Change to: At TMS, trace gases measurements of O3, CO and NO-NO2-NOx were made using commercial analyzers…”
Reply: Thanks for the suggestion. The text has been revised:
“At TMS, online measurements of O3, CO and NO-NO2-NOx were made using commercial analyzers.”
For details, please refer to lines 1-2, page 8 in the revised manuscript.

What is “regular internal calibration”? Please elaborate.
Reply: Thanks for the comment. To describe the calibration for the trace gas analyzers, the text was provided as follows:
“The O3 analyzer was calibrated by a transfer standard (Thermo Environmental Instruments (TEI) 49PS), while the other analyzers were calibrated daily by injecting scrubbed ambient air (TEI, Model 111) and a span gas mixture weekly with a NIST (National Institute of Standards and Technology) traceable standard (Scott-Marrin, Inc.), containing 156.5 ppmv CO (±2 %), 15.64 ppmv SO2 (±2 %), and 15.55 ppmv NO (±2 %), which was diluted using a dynamic calibrator (Envirionics, Inc., Model 6100).”
For details, please refer to lines 10-16, page 8 in the revised manuscript.

P7, L20: Change to: “For the O3, CO, NO and NOx analyzers…”
Reply: Thanks for the suggestion. The text has been changed accordingly:
“For the O3, CO, NO and NOx analyzers,…..”
For details, please refer to lines 16-17, page 8 in the revised manuscript.

At TMS, 1 min averaged data was collected, which at TW, hourly data were obtained
were the 1 min data subsequently averaged over the same interval as the TMS data? If so, please state this.
P7, L27: Change to “At TW, hourly O₃, CO, NO–NO₂–NOₓ and meteorological data were obtained…”

Reply: Yes, the hourly data obtained at TW were the 1-min data subsequently averaged over the same interval as the TMS data. The text was revised accordingly.

“At TW, hourly O₃, CO, NO–NO₂–NOₓ 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.”

For details, please refer to lines 24-26, page 8 in the revised manuscript.

P8, L4: What is PMF v3.0? Is this the U.S. EPA PMF 3.0 that you are using? If so, state appropriately and cite accordingly.

Reply: Thanks for the suggestion. PMF v3.0 is the version 3.0 of PMF. To state appropriately, the text was revised as follows:

“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.”

For details, please refer to line 2, page 9 in the revised manuscript.

P8, L17: Here you state that 16 compounds were included in the PMF analysis – a table with the additional compounds and the parameters used in the PMF should be included in the manuscript or as supplemental information. Furthermore, why weren’t these gases included as part of the whole analysis and simply limited to the PMF portion? It would be much more useful and informative to include time series plots of these gases and to also look at correlations to enhance the analysis and interpretation. Additionally, it would be instructive to include things like ethyne/CO, propane/ethane, toluene/benzene ratios to compare photochemical processing/air mass aging with that of the alkyl nitrates, particularly because you have samples from an urban and mountain site. While there are issues with being in directly in a source region regarding air mass age calculations using some of the hydrocarbons, utilizing the hydrocarbon data more fully will add to the analysis and potentially allow for a more thorough quantitative analysis of understanding the alkyl nitrate distributions – simply stating and re-stating that secondary formation is the dominant source of alkyl nitrates provides no new insight to our understanding of this class of compounds.

Reply: The reviewer’s excellent comment is highly appreciated. A table with the additional compounds and the parameters used in the PMF was provided as supplementary material (Table S1). In fact, we did use the same datasets to carry out in-depth data analysis and detailed interpretation of photochemical O₃ pollution,
photochemical ages of air masses, influence of different air masses, photochemical reactivity and/or the source apportionments of VOCs at the two sites in our previous papers (e.g., Guo et al., 2012a, 2012b, 2012c, 2013; Lam et al., 2013; Ling and Guo, 2014; Cheung et al., 2014; Ling et al., 2014; Wang et al., 2015). Therefore, in the present study, we only used the conclusions and findings of the previous papers wherever necessary, such as the influence of mesoscale circulation and regional transport, to avoid repetition and redundancy.

What do the distributions of MeCl and DMS look like and how do these differ on the ozone and non-ozone episode days? Can you back out enhancement ratios of MeCl to determine the influence of a local or regional biomass burning signal? In doing so, is this consistent with the PMF results for the alkyl nitrates? The fact that biomass burning was the second largest contributing factor in the PMF analysis for both sites would suggest that something like this is worth exploring, particularly because you have the MeCl data.

Reply: Thanks for the invaluable suggestion. We drew the time series of DMS and MeCl at TMS and TW (see Figure below). Indeed, high levels of DMS and CH$_3$Cl were frequently observed on both O$_3$ and non-O$_3$ episode days. The average concentrations of CH$_3$Cl on O$_3$ episode days were higher than those on non-O$_3$ episode days at TMS ($p < 0.05$), while the levels of CH$_3$Cl were comparable on O$_3$ and non-O$_3$ episode days at TW ($p > 0.05$).

![Time series of the mixing ratios of CH$_3$Cl and DMS at the TMS and TW. A color stripe has been added in the figure to highlight the O$_3$ episode days.](image)

To further understand the quantitative influence of biomass burning on the two sites,
we made significant revisions to the manuscript. For the TW site, we divided the sampling period into two categories — “meso” and “non-meso” scenarios for source apportionment analysis. The “meso” scenario included the nine high O$_3$ episode days with apparent mesoscale circulation, while the “non-meso” scenarios covered the rest of the sampling days. In other words, the “meso” scenario was mainly related to local sources while the “non-meso” was dominated by regional impact. Based on the two scenarios, the contributions of local and regional biomass burning to the TW site were obtained. For the TMS site, it was difficult to determine the relative contributions of biomass burning from local emissions and regional transport due to aged air masses mixed with several sources of alkyl nitrates. As a result, the discussion on biomass burning at the two sites was revised as follows:

“Since the air masses arriving at TMS were photochemically aged (Guo et al., 2013a), the source signatures of alkyl nitrates and their parent hydrocarbons were damaged at this mountain site. Therefore, only the data collected at the urban site were used for source apportionments of alkyl nitrates.” (Lines 27-30, page 21 and line 1, page 22 in the revised manuscript).

“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 O$_3$ 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 O$_3$ episode days with apparent mesoscale circulation, while the “non-meso” scenario covered the rest of the sampling days.” (Line 22, page 22 and lines 1-10, page 23 in the revised manuscript).

“It was found that in the “meso” scenario, secondary formation was the most significant contributor to the total alkyl nitrate 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). On the other hand, in 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 due to stronger photochemical reactions. Indeed, the PBM-MCM model simulation indicated that the average concentration of HO$_x$ (HO$_x$ = OH + HO$_2$) during daytime hours (0700-1800 LT) in the
“meso” scenario was \((2.5 \pm 0.7) \times 10^7\) molecule/cm\(^3\), about twice that of the “non-meso” scenario (Lines 19-30, page 23 and line 1, page 24 in the revised manuscript).

“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. The contribution of biomass burning in the “meso” scenario was likely attributable to the cooking/heating activities in the small villages nearby and the frequent barbecue activities at the foot of the mountain (Guo et al., 2013a, b), as well as the forest fire 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 peaks were not statistically different from the troughs. The difference of the average mixing ratio of \(\Sigma RONO_2\) between daytime and nighttime hours was only 1 pptv. The weak diurnal variations in the “non-meso” scenario suggests that the contribution of fresh biomass burning 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 (data not shown here). 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)” (Lines 10-22, page 24 and lines 1-8, page 25 in the revised manuscript).

For more details, please refer to Section 3.2.2 in the revised manuscript.

P8, L21-22: For the following: “…the performance of the model simulation was acceptable (Ling et al., 2011, 2014).”, while it is useful that you have included a citation for this statement, you should define/disseminate the criteria which make the results “acceptable” in the text so the reader can make their own judgement based on the facts. In this case, “acceptable” is subjective and I would recommend revising this to provide details of the analysis.

Reply: The reviewer’s comment is highly appreciated. In order to provide detailed information about the assessment of the PMF model performance, the following text was added in the manuscript:

“Different 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, good correlation between the observed and predicted VOC concentrations at TMS and TW (R\(^2\) = 0.99 and 0.98, respectively) was found 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. The Q values were stable and the Q values in the robust mode were approximately equal to the degrees of freedom (EPA, 2008; Friend et al., 2010). All the factors were mapped to a base factor in all the 100 runs in the bootstrapped simulation for the three-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).”

For details, please refer to lines 16-29, page 9 in the revised manuscript.

P9, L21: “forest” should be “forested”.

Reply: Revised as suggested.

For detail, please refer to line 15, page 11 in the revised manuscript.

P10, L8-11: geophysical should be either geographic or topographic The following sentence is an example of the generalizations used throughout the text regarding the distributions of the alky nitrates: “Nevertheless, the variations of RONO2 in a specific region were influenced by sampling conditions, meteorological parameters, geophysical features, direct emissions and secondary formation distributions, and sources and variations of parent hydrocarbons.” This is the case for alky nitrates everywhere…we already know this, the key is to hone in on the factors driving the spatial distributions at your sampling locations.

Reply: The reviewer’s comment is accepted. In the previous manuscript, we intended to provide a general description on the possible reasons for the different levels of RONO2 in different locations. The sentence has been deleted in the revised manuscript.

To find out the specific factors driving the spatial distributions at TW and TMS, we made significant revisions of the manuscript, including the source apportionments of alky nitrates, and the contributions of mesoscale circulation and regional transport.

As replied in the above comments, the above discussion, including a more specific interpretation of the results, has now been added in Section 3.2 in the revised manuscript.

P10, L14: Table 3 seems more appropriate as supplemental information. There is no real added value to the manuscript by including this in the main body. Additionally, the language used in several summaries is too casual – again, we’re back to saying that “the weather was fine” – purely subjective and not appropriate for a scientific manuscript.
Reply: Thanks for the suggestion. Table 3 has been deleted in the revised manuscript and put into the supplemental information as Table S2. We also tried to make the summaries more scientific.

P11, L9-10: change to “…peak values were observed in the afternoon…”
Reply: Revised as suggested:
“Although the ranges of alkyl nitrates mixing ratios were similar and peak values were observed in the afternoon,…”.
For detail, please refer to line 20, page 13 in the revised manuscript.

P11, L24-27: “Overall, the differences in the day-to-day variations of RONO2 resulted from differences in the contributions of direct emissions and secondary formation, levels of parent hydrocarbons, meteorological conditions and transport patterns (Guo et al., 2013a, b).”
Again, this says the exact same thing as P10, L8-11, but now we are dealing with temporal distributions! We already know these elements affect alkyl nitrate distributions; however, what new insight do the measurements from these two sites tell us about the driving factors in this area?
Reply: The valuable comment is highly appreciated. The sentence was deleted in the revised manuscript. Moreover, to provide new insight into alkyl nitrates in the revised manuscript, the discussion on the general characteristics of alkyl nitrates was re-written and re-organized, as replied earlier to the general comments. The general characteristics of alkyl nitrates, including the spatial and day-to-day variations, were highlighted to discuss the spatiotemporal differences of alkyl nitrates and their potential impact at the two sites in Section 3.1, while the actual driving factors, including the identification and quantification of sources, and the influence of mesoscale circulation and regional transport on O₃ episode and non-O₃ episode days, were analyzed in detail in Section 3.2.
For details, please refer to Section 3.1 and Section 3.2 in the revised manuscript.

P12, L2-5: Change to: Previous studies found that mesoscale circulation (mountain-valley breeze and regional transport) had a significant influence on the redistribution of air pollutants between the two sites (Guo et al., 2013a; Ling et al., 2014).”
Reply: Since Section 3.1 in the manuscript has been re-written and re-organized, the above sentence was deleted in the revised manuscript.

In this case, can you quantify “significant” for the reader? How do the results of these previous studies play in to what your measurements show? This is an area that could and should be expanded upon in order to understand the temporal distributions of the alkyl nitrates.

Reply: The reviewer’s valuable comment is greatly appreciated. To achieve this, as discussed above, in the revised manuscript, the quantitative influence of mesoscale circulation and regional transport was highlighted. For example, air samples were divided into two scenarios based on meteorological conditions and the levels of secondary air pollutants so as to investigate the source contributions of different air masses influenced by mesoscale circulation and/or regional transport at the urban site TW. On the other hand, the contributions of mesoscale circulation and regional transport to the alkyl nitrates at the mountain site TMS were quantified by the moving box model with Master Chemical Mechanism (Mbox).

For details, please refer to Section 3.2.2 and Section 3.2.3, pages 21-28 in the revised manuscript.

P12, L7-10: The following sentence makes it sound as though the fact that the alkyl nitrates were higher on ozone episode days was a new finding – this is typical, the C2 and higher alkly nitrates will track ozone, particularly during ozone events. Consider revising the following sentence to make note that this is a typical observation.

“In general, the diurnal variations of C2–C4 RONO2 on O3 episode days were larger and the mixing ratios were higher than those on non-O3 episode days at both sites (p< 0.05), confirming that secondary production of RONO2 was more significant on O3 episode days.”

Reply: Thanks for the comment. Since the discussion of the general characteristics of alkyl nitrates was re-written and re-organized, the above sentence was deleted in the revised manuscript. Instead, the following sentences were added:

“Typically, the average daytime levels of 2-PrONO2, 1-PrONO2 and 2-BuONO2 on high-level 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 C$_3$-C$_4$ alkyl nitrates which was photo-oxidation of parent hydrocarbons.” (Lines 2-11, page 14 in the revised manuscript).

“It was found that in the “meso” scenario, secondary formation was the most significant contributor to the total alkyl nitrate 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). On the other hand, in 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 due to stronger photochemical reactions. Indeed, the PBM-MCM model simulation indicated that the average concentration of HO$_x$ (HO$_x$ = OH + HO$_2$) during daytime hours (0700-1800 LT) in the “meso” scenario was (2.5 ± 0.7) $\times$ 10$^7$ molecule/cm$^3$, about twice that of the “non-meso” scenario.” (Lines 19-30, page 23 and line 1, page 24 in the revised manuscript).

For details, please refer to Section 3.1 and Section 3.2.2 in the revised manuscript.

P12, L12: change: “probably due to” to “likely resulting from”.

**Reply:** Thanks for the suggestion. Since the Section of the general characteristics of alkyl nitrates was re-written and re-organized, this sentence was deleted in the revised manuscript.

P12, L10-13: Regarding MeONO$_2$, what about the coastal and marine influences? This should at least be mentioned.

**Reply:** Thanks for pointing this out. As stated earlier, the diurnal variations of alkyl nitrates were deleted in the revised manuscript. However, we did provide the discussion on the influence of marine emissions in the revised manuscript as follows:

“At TW, however, besides the peak concentrations observed in the afternoon, ……, implying that the high levels of MeONO$_2$ and EtONO$_2$ might be 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 MeONO$_2$ and EtONO$_2$ levels at midnight - early morning on the above sampling days were related to oceanic emissions (see Section 3.2.2 for details).” (Lines 19-28, page 14 in the revised manuscript).
“For the oceanic emissions, a trough during daytime hours was found for ∑RONO₂ in the “meso” scenario, while a broad peak was present during daytime hours in the “non-meso” scenario. The daytime trough 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 due 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.” (Lines 9-18, page 25 in the revised manuscript).

“Moreover, the contributions of oceanic emissions to C₁-C₂ alkyl nitrates were higher than C₃-C₄ 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 C₁-C₂ alkyl nitrates, consistent with the results of previous work (Simpson et al., 2003).” (Lines 23-26, page 25 in the revised manuscript).

For details, please refer to Section 3.1, Section 3.2.2 and Figures 8-10 in the revised manuscript.

P13, L3-6: Revise to something like: “Although the diurnal variations of RONO₂ at Tai O during pollution episodes were similar to those observed in this study, with minimum values in the early morning and a broad peak in the afternoon, some differences were also observed.”

Reply: Thanks for the suggestion. As stated earlier, the discussion on the characteristics of alkyl nitrates at Tai O was shortened and the above sentence was deleted in the revised manuscript.


Reply: Thanks for the comment. As stated above, the discussion on the diurnal variations of alkyl nitrates at TMS, TW and Tai O was significantly shortened and the above wording was deleted in the revised manuscript.

P13, L12-14: For the following sentence: “This suggests that different RONO₂ shared common sources at Tai O, i.e., photochemical formation, while the source origins of RONO₂ in this study were more complicated.”

You state that the source origins of the alkyl nitrate were “more complicated” – first, what do you mean by more complicated? Based on your discussion of the diurnal profiles, how can you substantiate this statement? Different, sure, but I wouldn’t necessarily say more complicated. Furthermore, you state that photochemical
production is the dominant source of alkyl nitrates in the region – which is what was also driving the distributions at Tai O, so isn’t this statement contradictory to statements throughout the manuscript and the results from the PMF analysis? Additionally, more information needs to be provided in the manuscript regarding the Tai O measurements, particularly because the sampling for that study was heavily biased towards capturing high ozone events.

Reply: Sorry for the inappropriate expression. As replied earlier, the sampling method and sampling period at Tai O were different from those in the present study, which would bias the comparison of the data between Tai O and this study. Therefore, we only compared the levels of alkyl nitrates and their parent hydrocarbons at TMS and TW with those at Tai O and pointed out the limitation for comparison, while the comparison between observed ratios of alkyl nitrates/parent hydrocarbons and the predicted ratios, and the source apportionment of alkyl nitrates between Tai O and this study were all deleted in the revised manuscript.

Furthermore, the information of the sampling campaign at Tai O was added in the revised manuscript (Lines 11-20, page 6 and Lines 22-29, page 7).

P13: In general, I would recommend re-organizing section 3.2.

Reply: Thanks for the comment. Section 3.2 was substantially revised and re-organized as follows: The relationship of alkyl nitrates and their parent hydrocarbons was first explored to understand the influence of secondary formation and other sources on the levels of alkyl nitrates. Secondly, source apportionment of alkyl nitrates under two different scenarios (“meso” and “non meso”) at TW was conducted using the PMF model, while the contributions of mesoscale circulation and regional transport to the alkyl nitrates at TMS were quantified using the moving box model with Master Chemical Mechanism (Mbox) and the PBM-MCM model.

For details, please refer to Section 3.2 in the revised manuscript.

P14, L12-16: Revise to something such as: “The relationships between RONO2 and RH can be obtained by plotting the measured ratios of RONO2/RH to a specific ratio, 2-BuONO2/n-butane. The 2-BuONO2/n-butane has been used in this type of analysis because n-butane is typically one of the most abundant hydrocarbons and 2-BuONO2 is the most dominant alkyl nitrate (Roberts et al., 1998; Wang et al., 2013; Worton et al., 2010).
Reply: Thanks for the comment. The text has been revised accordingly:

“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 most dominant alkyl nitrate (Roberts et al., 1998; Wang et al., 2013; Worton et al., 2010).”

For details, please refer to lines 4-9, page 17 in the revised manuscript.

P14, L25&27: replace “drawn” with something like calculated, generated, obtained, etc.

Reply: “Drawn” was replaced by “generated” as follows:

“The curves generated with……., were generated by assuming that both photochemical formation…”

For details, please refer to lines 23-25, page 17 in the revised manuscript.

For the discussion that starts on P14 and continues on to P15, you need to introduce the figures into the text sooner in order to walk the reader through the key points.

Reply: Thanks for pointing this out. The introduction of the figures is now presented at the beginning of the discussion as follows:

“Figure 5 presents the relationships of C₁–C₃ RONO₂/RH to 2-BuONO₂/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 RONO₂/RH from 0000 to 0700 LT as the background initial ratio. Similarly, Figure 6 shows the relationships of C₁–C₃ RONO₂/RH to 2-BuONO₂/n-butane at TW.”

For details, please refer to lines 7-11, page 18 in the revised manuscript.

Also, Figure 6 (TMS and TW plots) should be introduced before Figure 5 (Tai O plots) based on how the section is written. Therefore, I’m going to refer to Figure 6 as Figure 5* and Figure 5 as Figure 6* for referencing. P15, L3-8: Revise to something like: “The BIR curves of C₁–C₃ RONO2 at both sites laid above their PP curves at shorter processing time (t < 1d) and converged towards the PP curves at longer processing times (t = 1.5–2 d) (Fig. 5*), resulting from the decreased influence of the parameter [RONO2]₀=[RH]₀e^(-(kA-kB)t) on the difference between the two curves as the photochemical age increased (Wang et al., 2013).

Reply: Sorry for the mistake. As mentioned earlier, the comparison of the observed ratios of alkyl nitrates/parent hydrocarbons with the predicted ratios at Tai O was deleted. Therefore, the old Figure 5, which presented the relationship of C₁–C₃
RONO₂/RH vs. 2-BuONO₂/n-butane at Tai O, was deleted accordingly.

In addition, the sentence mentioned above has been revised as follows:

“The BIR curves of C₁-C₃ alkyl nitrates at both sites laid 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 \( \frac{[RONO₂]₀}{[RH]₀} e^{(kₐₙₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐₐ¢

This section needs to be fleshed out in greater detail – additional discussion on the generation of the curves would be useful.

Reply: Thanks for the comments. An additional discussion on the generation of the curves was added in the revised manuscript:

“As photochemical oxidation of parent hydrocarbons is an important source of alkyl nitrates, it is helpful 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: ………. 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).”

For details, please refer to lines 5-29, page 16 and lines 1-27, page 17 in the revised manuscript.
P15-16, Section 3.2.2 needs a major overhaul – there are too many edits to make as it stands, but I would like to point out that references to Figures 5* and 6* need to be added in to the text to help clarify the discussion (essentially a blind discussion as written). Additionally, the authors simply present results but don’t provide any detailed discussion on the results from the three sites – more discussion on the variability of methyl and ethyl nitrate could be provided, and again, coastal and marine influences are neglected.

Reply: Thanks for the great comment. Section 3.2.2 has been significantly reorganized. In the revised manuscript, the analysis of the ratios of RONO₂ to parent hydrocarbons was deleted. Furthermore, the detailed discussion for the Tai O site was deleted (only mixing ratio comparison remained) as the revised manuscript only focused on the variations of alkyl nitrates and their sources and photochemical formation pathways at TMS and TW. On the other hand, Section 3.2.1 in the revised manuscript provides the comparison of the pure photochemical curves with the observed ratios at TMS and TW, indicating the influence of background levels and secondary formation on alkyl nitrates at the two sites, while the quantitative contributions of different sources, including oceanic emissions, biomass burning and secondary formation are now provided in the following Section (Section 3.2.2).

Please refer to Section 3.2.1 and Section 3.2.2 in the revised manuscript for details.

P16-17, Section 3.2.3: This is the section where I have the most concern in what is presented by the authors. When using the log-log plots of the alkyl nitrates to their parent hydrocarbon to estimate air mass age, by plotting the data on top of the calculated pure photochemical production line (effectively analogous to modeled result), the first point that needs to be made is that unless the data falls on the calculated line, you can’t use it to accurately assess an air mass age – this effectively says that the model and the measurements don’t agree, and we’re not accounting for all of the process appropriately. By adding in background mixing ratios of alkyl nitrates, we get better agreement because, in contrast to the pure photochemical production curves, there are background concentrations that aren’t accounted for in the pure photochemistry expression, especially for MeONO₂ and EtONO₂. Again, adding in background levels of alkyl nitrates provides a better “fit” to the data, but there are still other process occurring such as direct emissions and decomposition from larger organics that aren’t necessarily captured by these curves. The fact that the plots are log-log dampens the ability to observe subtle differences and variability.

The authors ultimately try to compare air mass ages based on the measurements using both the PP and BIR curves. In this section, which is a rather rudimentary discussion, they comment on how the air mass ages shift to longer “ages” in going from the PP
curve to the BIR curve. Unless the measurements are on the calculated line, it is not appropriate to make statements that air mass ages are changing based on which curve you use. While the differences in air mass ages aren’t large, the point is that in order to meaningfully use this as a comparative tool, the data and the calculated curve must agree. What should be addressed (and partially is in the following section) is the magnitude of deviations from the PP and BIR curves and what are the key drivers. Additionally, because the expressions used to generate the PP and BIR curves approach convergence at longer processing times, it is not surprising that the more processed air masses are in better agreement with the PP and BIR curves.

Thus, the point of the following paragraph is not clear, and what I observe in the plots and what is in the text do not appear to be the same

“Figure 5* presents the relationship between C1–C3 RONO2/RH and 2-BuONO2/n-butane based on the measured values of C1–C4 RONO2 and RH at TMS and TW. The photochemical age shown by the PP curves for the whole sampling period ranged from 6 h to 2 days at TMS, compared to < 30min to 18 h at TW. However, when BIR curves were used, the photochemical age of air masses at TMS became 30min to 1.5 days, yet it remained the same at TW. The similar photochemical age shown by both the PP and BIR curves at TW implies that the increment of RONO2 during daytime hours was mainly due to the oxidation of locally emitted precursors (Cheung et al., 2014).”

For the last sentence, “The similar photochemical age shown by both the PP and BIR curves at TW implies that the increment of RONO2 during daytime hours was mainly due to the oxidation of locally emitted precursors (Cheung et al., 2014).”, I don’t see that the PP and BIR curves are the same for any of the alkyl nitrate/parent hydrocarbon ratios in Figure 5*, and how does this substantiate that the levels observed were from locally emitted sources? If you were to take an upper limit of 18 hours and the average wind speed for the region, what area would that cover in relation to source regions for the air masses sampled? My guess is that it wouldn’t all be local.

**Reply:** The reviewer’s valuable comments are highly appreciated, which helps advance our understanding of the use of the comparison between observed ratios and the pure photochemical curves/background initial ratio curves. As large deviations were found between the observed ratios and the pure/photochemical curves/background initial ratio curves, it is inappropriate to use the plots to explain the photochemical ages of air masses at the two sites. Therefore, the above discussion on the photochemical ages of air masses using the plots of observed ratios of RONO2/RH vs. 2-BuONO2/n-butane with those of pure photochemical curves and background initial ratio curves was totally deleted.

According to the reviewer’s comments, the comparison of the observed ratios of
RONO$\textsubscript{2}$/RH vs. 2-BuONO$\textsubscript{2}$/n-butane with the theoretical ratios in the pure photochemical (PP) curves and background initial ratio (BIR) curves was substantially revised. The deviations between the observed and theoretical ratios and the implication are now provided in the revised manuscript as follows, and are used to indicate the influence of photochemical formation and sources other than secondary formation on alkyl nitrates.

“At TMS, the measured ratios of MeONO$\textsubscript{2}$/methane and EtONO$\textsubscript{2}$/ethane to 2-BuONO$\textsubscript{2}$/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$\textsubscript{2}$/RH to 2-BuONO$\textsubscript{2}$/n-butane were influenced by aged air masses due to long atmospheric lifetimes and slow photochemical degradation 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$\textsubscript{2}$/RH to 2-BuONO$\textsubscript{2}$/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). Indeed, our previous field measurements at Hok Tsui, a PRD regional background site, presented average MeONO$\textsubscript{2}$ and EtONO$\textsubscript{2}$ mixing ratios of 10.4 ± 0.7 and 9.6 ± 0.7 pptv (non-published data, 2001-2002), respectively, which were non-negligible values.”

For details, please refer to lines 8-20, page 19 and lines 1-3, page 20 and the last paragraph in Section 3.2.1 in the revised manuscript.

P17, L2-3: “This was consistent with the photochemical age of air masses at TMS, suggesting that the air masses arriving at the two sites were complex.”

How do complex air masses translate into consistent photochemical air mass ages at Tai O and TMS?

Reply: Thanks for the reviewer’s comment. As mentioned above, the discussion of photochemical ages using plots of RONO$\textsubscript{2}$/RH vs 2-BuONO$\textsubscript{2}$/n-butane and the photochemical ages at Tai O was deleted.

P17, L12: “brought to TMS” should be “transported to TMS”

Reply: Thanks for the reviewer’s suggestion. As mentioned, the discussion of photochemical ages using plots of RONO$\textsubscript{2}$/RH vs 2-BuONO$\textsubscript{2}$/n-butane was deleted.
Section 3.2.4 – change/add the figure numbers accordingly.

In addition to the ratios of RONO$_2$/RH and the photochemical age of air masses, a comparison of the measured ratios of C$_1$–C$_3$ RONO$_2$/RH to 2-BuONO$_2$/n-butane and PP and BIR curves could provide useful information about the evolution of RONO$_2$ at the two sites (Fig. 5*).

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 (Fig. 5*a,b), with the trends approaching the PP curves at a longer processing time of 1.5–2 days.

Reply: Thanks for pointing this out. As the manuscript has been revised, the number of figures has been re-ranked accordingly.

“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.”

Please refer to lines 8-10, page 19 in the revised manuscript for details.

You do not need to say that you have confirmed the existence of background levels of ambient RONO$_2$ – this is already demonstrated by the minimum/lowest quartile/percentile values at your sites.

Reply: Thanks for the reviewer’s suggestion. The text has been revised accordingly:

“Indeed, our previous field measurements at Hok Tsui, a PRD regional background site, presented average MeONO$_2$ and EtONO$_2$ mixing ratios of 10.4 ± 0.7 and 9.6 ± 0.7 pptv (non-published data, 2001-2002), respectively, which were non-negligible values.”

For details, please refer to line 20, page 19 and lines 1-3, page 20 in the revised manuscript.

P18, L29: “analyzed” should be “examined”.

Reply: Thanks for pointing this out. The “analyzed” was replaced by “examined”:

“……the ratio of 1-/2-PrONO$_2$ was examined…”

For detail, please refer to line 22, page 20 in the revised manuscript.

P20, L1-7: “However, in addition to C3 RONO2, the tendencies of the observed ratios of C1–C2 RONO2/RH to 2-BuONO2/n-butane showed the same patterns as the BIR curves at Tai O, which were different from those at TMS and TW, suggesting that photochemical oxidation had a significant influence on the variations of RONO2 at Tai O (Simpson et al., 2006).”

This is because the Tai O samples were biased from sampling ozone episodes, yet this
isn’t mentioned and is a critical point. Please address.

Reply: Thanks for the comment. Since the manuscript has been reorganized, the above description of the comparison of the observed ratios of RONO$_2$/RH vs 2-BuONO$_2$/n-butane with the predicted ones in the PP and BIR curves at Tai O has been deleted.

P20, L16: “Figure 6” should actually be “Figure 7”.

Reply: The number of the figures has been re-ranked accordingly.

P21, L25-27: The manuscript ends abruptly here, yet one thing that I do find curious is that at Tai O, the secondary formation and biomass burning factors were statistically equal, and marine influence did not come into play at all. There is no discussion here, simply reiterating results, but yet again, are these results driven by the fact that the Tai O sampling was biased?

Reply: Thanks for the good comment. As mentioned earlier, the discussion about source apportionment of Tai O was deleted in the revised manuscript. Instead, the detailed discussion of the source apportionments of alkyl nitrates at Tai O was provided in our paper (Lyu et al., 2015).

P22, L16: Confirming the existence of background levels of RONO$_2$ and RH at both sites is not a conclusion – please omit.

Reply: Thanks for the suggestion. The above description has been deleted. Furthermore, the whole conclusion section has been revised as follows:

“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 foot 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 remarkable 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, on the days with mesoscale circulations the photo-oxidation of parent hydrocarbons from TW accounted for 52-85% of the alkyl
nitrates at TMS, while on the days with regional impact, alkyl nitrates from the inland PRD region were the major contributor to alkyl nitrate levels at TMS, with a percentage contributions of 58-82%. The photo-oxidation of parent hydrocarbons from TW and regional transport led to the similar values of alkyl nitrates observed at the two sites. With regard to the secondarily formed alkyl nitrates, the reaction of RO₂ and NO was the prominent pathway at both sites. Moreover, the formation of alkyl nitrates made negative contributions to the O₃ formation, with a reduction rate of -4.1 and -4.7 pptv O₃ per pptv alkyl nitrates at TMS and TW, respectively. The findings of this study are expected to advance the understanding on the source contributions and the impact factors of alkyl nitrates in mountainous areas in Hong Kong."

For details, please refer to the conclusion section, page 30 in the revised manuscript.

The overall quality of the figures needs to be improved greatly. I would encourage the authors to change the figure fonts Sans Serif fonts because they are easier to read, especially when small. Figure 1 – add in Tai O on the map for reference. Figure 3 – add in other gases, such as the parent hydrocarbons? Increase font size on both x- and y-axis. Add a stripe of color over the ozone episode days in order to highlight/distinguish these events. Figure 4 – I would re-order and have MeONO₂ at the top and 2-BuONO₂ at the bottom. Also, what do the parent hydrocarbon diurnal cycles look like?

Reply: Thanks for the comment. The figures were revised accordingly. All figures now use a sans serif font. The location of Tai O was added in Figure 1. In addition, the time series of the parent hydrocarbons were provided in a new figure — Figure 4 in the revised manuscript. Furthermore, the font sizes in both x- and y-axis were increased as much as possible. A stripe of color was also provided in Figures 3 & 4 to highlight the O₃ episode days. On the other hand, as the manuscript has been revised and re-organized, the diurnal patterns of alkyl nitrates and their parent hydrocarbons were deleted in the revised manuscript.

Figures 5 & 6: The TW and TMS figure should be Figure 5 and the Tai O plots should be Figure 6. For both Figures 5 and 6, the panels should be in the same order so that it’s easy for the reader to look at both figures and compare the appropriate gases. Also, a legend is needed for figures 5 and 6, particularly 5 (TW and TMS) – all plots need to be larger in size, have larger symbols that are easier to differentiate, and also add in TW and TMS over the clusters of data points for figure 5.

Reply: Thanks for the comments. In the revised manuscript, the plot for the observed ratios of RONO₂/RH vs 2-BuONO₂/n-butane at Tai O was deleted. On the other hand, the plots for the observed ratios of RONO₂/RH vs 2-BuONO₂/n-butane at TMS and
TW were presented individually (Figures 5 and 6 in the revised manuscript). Legends have been added into the figures, fonts have been changed from serif to sans serif, and the font size and symbol size were increased as much as possible.
For details, please refer to Figures 5 and 6 in the revised manuscript.

At last, we would like express our sincere thanks to the reviewers for their time, patience and efforts on the review of our manuscript.
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 (TMS) and an urban site (TW) at the foot 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 different elevations of the sites, suggesting different source contributions of alkyl nitrates at the two sites, which was proved by the analysis of photochemical evolution of alkyl nitrates. 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. On the other hand, alkyl nitrates at TMS were mainly due to the photo-oxidation of parent hydrocarbons at TW when mesoscale circulation, i.e., valley breezes occurred, contributing 52-86% to the levels of alkyl nitrates at TMS. In contrast, 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 nitrous 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 (RONO$_2$) are important photochemical pollutants in the atmosphere due to their roles in local, regional and global atmospheric chemistry (Jenkin et al., 2000; Seinfeld and Pandis, 2006). Alkyl nitrates are reactive nitrogen compounds (NO$_y$) and act as a critical reservoir of nitrogen oxides (NO$_x$ = NO + NO$_2$) during long-range transport due to 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 NO$_2$ (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):

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

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 NO$_2$, subsequently leading to O$_3$ production by NO$_2$ photolysis. Therefore, alkyl nitrates are often used as indicators of photochemical O$_3$ 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 RONO$_2$/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):

\[ RONO_2 + h\nu \rightarrow RO^- + NO_2, J_{RONO2}, (R6) \]
\[ RONO_2 + OH \rightarrow \text{products}, k_6, (R7) \]

where \( h\nu \) is sunlight and \( J_{RONO2} \) 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 (Clemishaw 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 \( O_3 \) 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. \( C_3-C_4 \) 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 (\( CH_3O^- \)) reaction with \( NO_2 \) was a viable alternative pathway for the observed high levels of MeONO\(_2\) 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 foot 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, i.e., 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 foot 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 15-20 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. Due to 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). Further to the east are the urban areas, with a straight distance of 32 km, and to the northeast, north and northwest is the polluted PRD region. The Asian monsoon has a significant influence on the seasonal variations of air pollutants at Tai O. In autumn and winter, prevailing northerly winds bring anthropogenic emissions from the PRD region to Tai O, which superimpose with emissions from local urban areas. In summer, clean oceanic air masses dilute the levels of air pollutants because of the influence of dominant southerly winds. 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 O₃ episode days and 10 non-O₃ episode days using evacuated 2-L stainless steel canisters. Each of the collected canister samples was integrated over a 60-min sampling duration. A total of 384 samples were collected at the two sites. The O₃ episode days were selected as the days with the highest daytime hourly O₃ level at a regional scale (higher than 100 ppbv), which were based on weather forecasts and meteorological data analysis, and confirmed by the observed O₃ mixing ratios. During non-O₃ episode days, one-hour integrated samples were collected at 2-h intervals from 0700 to 1900 local time (LT) (7 samples per day). On O₃ 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 C₁, C₂, C₃ and C₄ 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 O₃, CO and NO-NO₂-NOₓ
At TMS, online measurements of O₃, CO and NO-N₂O⁻NOₓ were made using commercial analyzers. O₃ was measured using a commercial UV photometric instrument (Advanced Pollution Instrumentation (API), model 400E) that has a detection limit of 0.6 ppbv. CO 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 (CO₂) for baseline determination. The detection limit was 30 ppbv for a 2-min average. The 2s precision was about 1% for a level of 500 ppbv (2-min average) and the overall uncertainty was estimated to be 10%. NO, NO₂ and NOₓ were detected with a chemiluminescence NO-N₂O⁻NOₓ analyzer (API, Model 200E) that had a detection limit of 0.5 ppbv. The O₃ analyzer was calibrated by a transfer standard (Thermo Environmental Instruments (TEI) 49PS), while the other analyzers were calibrated daily by injecting scrubbed ambient air (TEI, Model 111) and a span gas mixture weekly with a NIST (National Institute of Standards and Technology) traceable standard (Scott-Marrin, Inc.), containing 156.5 ppmv CO (±2 %), 15.64 ppmv SO₂ (±2 %), and 15.55 ppmv NO (±2 %), which was diluted using a dynamic calibrator (Environics, Inc., Model 6100). For the O₃, CO, NO and NOₓ analyzers, a data logger (Environmental Systems Corporation Model 8816) was used to control the calibrations and to collect data, which were averaged to 1-min values.

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 O₃, CO, NO-N₂O⁻NOₓ 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.
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 CH$_3$Cl was specifically used for biomass burning. DMS was a typical tracer for marine emissions, while O$_x$ (i.e., O$_3$ + NO$_2$) was used as the tracer of secondary formation through photochemical reactions including the formation of alkyl nitrates because O$_3$ shares a common photochemical source with alkyl nitrates (Simpson et al., 2006). In addition to the aforementioned species, alkyl nitrate precursors, including methane, propane and n/i-butanes, were input into the model. In total, sixteen compounds were used for the model input. Different 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, good correlation between the observed and predicted VOC concentrations at TMS and TW ($R^2 = 0.99$ and 0.98, respectively) was found 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. The Q values were stable and the Q values in the robust mode were approximately equal to the degrees of freedom (EPA, 2008; Friend et al., 2010). All the factors were mapped to a base factor in all the 100 runs in the bootstrapped simulation for the three-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 alkyl nitrates (Ling et al., 2011; Ling and Guo, 2014).

2.5. Photochemical box model incorporating master chemical mechanism
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-PrONO₂ and 2-BuONO₂ 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\textsubscript{2} and 2-BuONO\textsubscript{2} were due to 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\textsubscript{2}, EtONO\textsubscript{2} and 2-PrONO\textsubscript{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\textsubscript{2} and 2-BuONO\textsubscript{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\textsubscript{1}-C\textsubscript{3} alkyl nitrates were slightly lower and the 2-BuONO\textsubscript{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 O\textsubscript{3} 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 EtONO$_2$, 1-PrONO$_2$ and 2-BuONO$_2$ were slightly higher and the MeONO$_2$ and 2-PrONO$_2$ 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></th>
<th>TW</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean*</td>
<td>Min.</td>
<td>Max.</td>
<td>Mean</td>
</tr>
<tr>
<td>MeONO$_2$</td>
<td>10.9 ± 0.4</td>
<td>6.2</td>
<td>21.4</td>
<td>12.6 ± 0.5</td>
</tr>
<tr>
<td>EtONO$_2$</td>
<td>12.1 ± 0.5</td>
<td>3.2</td>
<td>25.6</td>
<td>13.3 ± 0.6</td>
</tr>
<tr>
<td>2-PrONO$_2$</td>
<td>24.1 ± 1.1</td>
<td>4.0</td>
<td>51.2</td>
<td>26.3 ± 1.2</td>
</tr>
<tr>
<td>1-PrONO$_2$</td>
<td>3.8 ± 0.2</td>
<td>0.4</td>
<td>10.6</td>
<td>4.0 ± 0.2</td>
</tr>
<tr>
<td>2-BuONO$_2$</td>
<td>32.0 ± 1.7</td>
<td>3.1</td>
<td>80.1</td>
<td>34.2 ± 1.9</td>
</tr>
<tr>
<td>Methane (ppmv)</td>
<td>2.0 ± 0.1</td>
<td>1.8</td>
<td>2.2</td>
<td>2.0 ± 0.1</td>
</tr>
<tr>
<td>Ethane</td>
<td>1908 ± 78</td>
<td>396</td>
<td>3588</td>
<td>2224 ± 90</td>
</tr>
<tr>
<td>Propane</td>
<td>1101 ± 75</td>
<td>106</td>
<td>4455</td>
<td>3551 ± 415</td>
</tr>
<tr>
<td>n-Butane</td>
<td>830 ± 91</td>
<td>97</td>
<td>6252</td>
<td>4486 ± 482</td>
</tr>
</tbody>
</table>

* Average ± 95% confidence interval

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 S1 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, weather 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 weather conditions with high-pressure system and/or stable weather 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 peak values were observed in the afternoon, the day-to-day variations of individual alkyl nitrates differed during the sampling period at both sites. The peak values were comparable and the diurnal patterns well tracked each other for 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, respectively, on the non-O₃ episode days. Typically, the average daytime levels of 2-PrONO₂, 1-PrONO₂ and 2-BuONO₂ on high-level 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 parent hydrocarbons. For C₁-C₂ alkyl nitrates, the patterns of peaks and troughs 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 indicative of photo-oxidation of methane and ethane, apart from potential influence of air masses in upwind areas due to regional transport (Guo et al., 2009; Jiang et al., 2010) and/or mesoscale circulations (Gao et al., 2005; Wang et al., 2006). At TW, however, besides the peak 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 might be 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. Time series of MeONO$_2$, EtONO$_2$, 1-PrONO$_2$, 2-PrONO$_2$ and 2-BuONO$_2$ measured at TMS (purple) and TW (red) in 2010. The yellow shading highlights the O$_3$ episode days.

Figure 4. Time series of the parent hydrocarbons of alkyl nitrates at TMS and TW. The yellow shading highlights the O$_3$ episode days.

Overall, though the levels of the parent hydrocarbons were lower at TMS, similar values of alkyl nitrates were observed at both sites regardless of different elevations of the sites, suggesting the contributions of different sources and/or the influence 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 O₃ and alkyl nitrates were in-depth studied 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 helpful 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 NOₓ-rich, making the reaction with NO being the dominant pathway for the destruction of RO₂ radicals (Russo et al., 2010). In this study, the average mixing ratios of NOₓ at TMS and TW were 10.7 ± 0.3 and 56.3 ± 1.6 ppbv, respectively, indicating that the environment was NOₓ-rich (> 0.1 ppbv, Roberts et al., 1998). Hence, reaction with NO was the main pathway for the destruction of RO₂ 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).

\[
\frac{[RONO]}{[RH]} = \frac{\beta k_A}{k_B - k_A} (1 - e^{(k_A - k_B) \tau}) + \frac{[RONO]_0}{[RH]_0} e^{(k_A - k_B) \tau} \quad \text{(Eq. 1)}
\]

where \( \beta = \alpha_1 \alpha_2 \), \( k_A \) 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. \([OH]\) 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):

\[
\frac{RONO}{RH} = \frac{B\alpha}{k_B - k_A} \left(1 - e^{k_A \cdot t_B \cdot x} \right)
\]  \quad (2)

The relationships between alkyl nitrates and RH are obtained by plotting the measured ratios of RONO$_2$/RH to a specific ratio, 2-BuONO$_2$/n-butane. The 2-BuONO$_2$/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-BuONO$_2$ is the most 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 RONO$_2$/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 [OH] were simulated using the PBM-MCM (Lyu et al., 2016). By providing the values of photochemical processing time \(t\), the predicted ratios of RONO$_2$/RH were calculated since other parameters, i.e., \(k_A, k_B, \alpha_1, \alpha_2\) and \(J_{RONO2}\) could be obtained from literatures (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 laid
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 $\frac{[\text{RONO}_2]_0}{[\text{RH}]_0} e^{(k_{t,k})t}$ 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](image-url)  
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 C1-C3 RONO2/RH with 2-BuONO2/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 RONO2/RH from 0000 to 0700 LT.

At TMS, the measured ratios of MeONO2/methane and EtONO2/ethane to 2-BuONO2/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 C1-C2 RONO2/RH to 2-BuONO2/n-butane were influenced by aged air masses due to long atmospheric lifetimes and slow photochemical degradation 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 C1-C2 RONO2/RH to 2-BuONO2/n-butane in BIR curves was comparatively smaller, further confirming that there were other sources contributing to ambient C1-C2 alkyl nitrates besides photochemical formation, including the background levels of C1-C2 alkyl nitrates and their parent hydrocarbons (direct measurements of RH in Table 1) (Wang et al., 2013). Indeed, our previous field measurements at Hok Tsui,
PRD regional background site, presented average MeONO$_2$ and EtONO$_2$ mixing ratios of 10.4 ± 0.7 and 9.6 ± 0.7 pptv (non-published data, 2001-2002), respectively, which were non-negligible values.

With regard to 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 revealing 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-BuON$_2$/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 closer to the ratios of the BIR curve than those of the PP curve (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 due to 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 due to 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 $\beta_{1\text{-PrONO}_2}/\beta_{2\text{-PrONO}_2}$ (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), confirming the existence 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). Indeed, 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 errors in the figure were obtained from a bootstrap analysis of the PMF model simulation. Since the air masses arriving at TMS were photochemically aged (Guo et al., 2013a), the source signatures of alkyl nitrates and their parent hydrocarbons were damaged at this mountain site. Therefore, only the data collected at the urban site were used for source
apportionments of alkyl nitrates.

High concentrations of O₃ 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, n/i-butanes, benzene and CO were present in this factor. It is not surprising that O₃ correlated with the aforementioned species given that O₃ 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 n/i-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 n/i-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, the total concentrations of alkyl nitrates 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 absolute concentration at TW, respectively. The mixing ratios of total alkyl nitrates (i.e., \( \sum \text{RONO}_2 = \text{MeONO}_2 + \text{EtONO}_2 + 1\text{-PrONO}_2 + 2\text{-PrONO}_2 + 2\text{-BuONO}_2 \)) 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 nitrate 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). On the other hand, in 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 due to stronger 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/cm$^3$, 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 absolute concentration).

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 the cooking/heating activities in the small villages nearby and the frequent barbecue activities at the foot of the mountain (Guo et al., 2013a, b), as well as the forest fire 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 peaks were not statistically different from the troughs. The difference of the average mixing ratio of $\Sigma$ RONO$_2$ between daytime and nighttime hours was only 1 pptv. The weak
diurnal variations in the “non-meso” scenario suggests that the contribution of fresh biomass burning 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 (data not shown here). 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 trough during daytime hours was found for \( \Sigma \text{RONO}_2 \) in the “meso” scenario, while a broad peak was present during daytime hours in the “non-meso” scenario. The daytime trough 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 due 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.

Moreover, the contributions of oceanic emissions to \( \text{C}_1-\text{C}_2 \) alkyl nitrates were higher than \( \text{C}_3-\text{C}_4 \) 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 \( \text{C}_1-\text{C}_2 \) alkyl nitrates, consistent with the results of previous work.

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

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(Simpson et al., 2003). Instead, 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 brought freshly-emitted parent hydrocarbons and alkyl nitrates from the urban areas at the foot 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). Indeed, except 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 gradually undertaken, and eventually contributed to the ambient alkyl nitrates at TMS. As such, the model was only constrained with the observed daytime data at TW. On the other hand, the air masses flew down the mountain due to 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 valley breeze occurred. The average mixing ratios of MeONO₂, EtONO₂, 1-PrONO₂,
2-PrONO\textsubscript{2} and 2-ButONO\textsubscript{2} at daytime hours estimated using the Mbox model were accounted for 86%, 52%, 66%, 65% and 86% of the observed values at TMS during the same period, respectively, demonstrating that when there was mesoscale circulation, the levels of alkyl nitrates at TMS were dominated by the photo-oxidation of their parent hydrocarbons originated at 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.

For the “non-meso” scenario, the simulated levels of in-situ formation of MeONO\textsubscript{2}, EtONO\textsubscript{2}, 1-PrONO\textsubscript{2}, 2-PrONO\textsubscript{2} and 2-BuONO\textsubscript{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\textsubscript{1}-C\textsubscript{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. Indeed, 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 firmly confirmed in Guo et al. (2013a). Hence, by excluding the locally-formed alkyl nitrates from the overall levels of alkyl nitrates, we obtained the contribution of regional sources to alkyl nitrates at TMS. The regional source contributions to MeONO\textsubscript{2}, EtONO\textsubscript{2}, 1-PrONO\textsubscript{2}, 2-PrONO\textsubscript{2} and 2-BuONO\textsubscript{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 at TMS. It is noteworthy that the regional alkyl nitrates included those photochemically formed and emitted from biomass burning and oceanic sources in that the inland PRD region.
Table 3. Mixing ratios of C$_1$-C$_4$ alkyl nitrates influenced by mesoscale circulation ("Meso"), in-situ formation and regional transport at TMS (unit: pptv).

<table>
<thead>
<tr>
<th>Scenario</th>
<th>MeONO$_2$</th>
<th>EtONO$_2$</th>
<th>1-PrONO$_2$</th>
<th>2-PrONO$_2$</th>
<th>2-BuONO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;Meso&quot;</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 O$_3$

Alkyl nitrates are mainly formed through the reaction of peroxy radical (RO$_2$) and NO. However, NO can be oxidized by RO$_2$ to form NO$_2$, which results in tropospheric O$_3$ formation through NO$_2$ photolysis. Hence, investigating the relationship between alkyl nitrates and O$_3$ is of help to evaluate the influence of alkyl nitrates on O$_3$ formation (Simpson et al., 2006). Since photochemical formation of O$_3$ and alkyl nitrates occurs during daytime hours, the relationship between O$_3$ and alkyl nitrates is usually evaluated using the observed daytime data (i.e., 0900-1600 LT). In this study, the mixing ratios of O$_x$ were used to recover the loss of O$_3$ due to the NO titration. Figure 11 shows the correlation between O$_x$ and the total alkyl nitrates ($\Sigma$ RONO$_2$) at daytime hours. Good correlations were found at TMS ($R^2 = 0.63$) and TW ($R^2 = 0.56$) 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 RO$_2$ and NO, 0.67 and 0.47 ppbv of O$_x$ could be simultaneously produced at TMS and TW, respectively. The relatively higher slope at TMS than at TW was owing to higher concentrations of HO$_x$ radicals and higher photochemical reactivity of VOCs at TMS (Lyu et al., 2016). In addition, as the formation of alkyl nitrates consumes NO, it resulted in negative contribution to O$_3$ formation. To quantify the negative influence on O$_3$, the PBM-MCM model was applied to the whole data collected at TMS and TW, respectively (Lyu et al., 2016). It was obvious that the formation of alkyl nitrates made negative contributions to the O$_3$ 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 O$_3$ for the formation of MeONO$_2$, EtONO$_2$, 1-PrONO$_2$, 2-PrONO$_2$ and 2-BuONO$_2$ 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.

![Figure 11. Correlation between Oₓ (O₃ + NO₂) and total alkyl nitrates at (a) TMS and (b) TW.](image)

Moreover, because secondary alkyl nitrates are formed through two main reaction pathways, *i.e.*, “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 simulation 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. The 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 foot 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 remarkable 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, on the days with mesoscale circulations the photo-oxidation of parent hydrocarbons from TW accounted for 52-85% of the alkyl nitrates at TMS, while on the days with regional impact, alkyl nitrates from the inland PRD region were the major contributor to alkyl nitrate levels at TMS, with a percentage contributions of 58-82%. The photo-oxidation of parent hydrocarbons from TW and regional transport led to the 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 are expected to advance the understanding on the source contributions and photochemical formation pathways of alkyl nitrates in mountainous areas in Hong Kong.

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<table>
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<th>Group</th>
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<th>TW (ppbv)</th>
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<td></td>
<td>1,2,3-trimethylbenzene</td>
<td>0.01 ± 0.01</td>
<td>0.03 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>1,2,4-trimethylbenzene</td>
<td>0.03 ± 0.01</td>
<td>0.11 ± 0.02</td>
</tr>
<tr>
<td></td>
<td>1,3,5-trimethylbenzene</td>
<td>0.02 ± 0.01</td>
<td>0.04 ± 0.01</td>
</tr>
<tr>
<td>Isoprene</td>
<td></td>
<td>0.11 ± 0.02</td>
<td>0.24 ± 0.03</td>
</tr>
<tr>
<td>CO</td>
<td></td>
<td>436 ± 7</td>
<td>517 ± 8</td>
</tr>
<tr>
<td>NO_\text{x}</td>
<td></td>
<td>10.7 ± .3</td>
<td>55 ± 1</td>
</tr>
<tr>
<td>O_3</td>
<td></td>
<td>55 ± 1</td>
<td>22 ± 1</td>
</tr>
<tr>
<td>O_\text{x} (O_3+NO_2)</td>
<td></td>
<td>58 ± 1</td>
<td>47 ± 1</td>
</tr>
</tbody>
</table>

* Mean ±95% confidence intervals
Table S2. Summary of synoptic weather conditions and the corresponding variations of air pollutants on the sampling O$_3$ and non-O$_3$ episode days.

<table>
<thead>
<tr>
<th>Sampling days</th>
<th>Synoptic weather conditions</th>
<th>Variation of pollutants</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>O$_3$ episode day</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>October 23~24 2010</td>
<td>After the tropical cyclone Megi, the weather was sunny. The temperature (max: 23 and 31 °C at TMS and TW, respectively) and solar radiation levels (max: 843 and 851 W/m$^2$, respectively) increased and remained at high levels. The wind speed decreased and the prevailing wind direction was from the north at TMS. The prevailing winds at TW changed from southeast on October 23 to north on October 24.</td>
<td>O$_3$, NO and SO$_2$ increased clearly and CO increased moderately. O$_3$ reached peaks of 137 ppbv at TMS and 85 ppbv at TW. SO$_2$ reached 10 ppbv at TMS and 14 ppbv at TW. The mixing ratios of alkyl nitrates increased clearly and the diurnal patterns of alkyl nitrates were more significant with peak values observed in the afternoon. The diurnal patterns tracked each other well for C$_3$-C$_4$ alkyl nitrates at TMS and TW.</td>
</tr>
<tr>
<td>October 29 ~ November 3, 2010</td>
<td>With a continental anticyclone over mainland China, the temperature started to increase and the weather was sunny. A northerly dry monsoon was enhanced at both sites. The solar radiation levels were higher at TMS than that at TW, where their peaks reached 811 and 800 W/m$^2$, respectively. The winds were mostly from the north at TMS, and those at TW were from the southeast, east and northeast.</td>
<td>O$_3$ increased and stayed at high levels at TMS. SO$_2$ and CO at the two sites exhibited an increasing trend and a broad peak. The levels of alkyl nitrates were slightly lower than those on October 23 and 24 at both sites. The diurnal patterns of C$_1$-C$_2$ alkyl nitrates with troughs and peaks during daytime hours were observed on October 29 - November 3 at both sites.</td>
</tr>
<tr>
<td>November 9, 2010</td>
<td>A continental anticyclone controlled northwestern China. After rainy days on November 4 ~ 6, the weather was sunny and stable. The temperatures and solar radiation levels increased and the wind speeds decreased.</td>
<td>O$_3$ stayed at a level above 100 ppbv at TMS. NO remained stable and the levels of CO and SO$_2$ fluctuated. The levels of alkyl nitrates increased significantly at TMS and TW, with peaks observed in the afternoon.</td>
</tr>
<tr>
<td>November 19, 2010</td>
<td>The anticyclone moved over northeastern China and the East China Sea. Although the prevailing direction was from the north at both sites, the wind speeds decreased. The solar radiation levels were higher at TMS than those at TW, with maximum values of 673 and 555 W/m$^2$, respectively.</td>
<td>O$_3$ increased sharply and reached peaks higher than 110 ppb at TMS. CO had a broad peak at both sites. The peak values of alkyl nitrates increased significantly. C$_3$ and C$_4$ alkyl nitrates peaked in the afternoon at the two sites. The maximum MeONO$_2$ and EtONO$_2$ levels were observed at midnight at TW and in the afternoon at TMS on some sampling days.</td>
</tr>
</tbody>
</table>

**Non-O$_3$ episode days**
<table>
<thead>
<tr>
<th>Date/Region</th>
<th>Weather/Conditions</th>
<th>O$_3$ and Alkyl Nitrates</th>
</tr>
</thead>
<tbody>
<tr>
<td>September 28, October 2, 8, 14, 2010</td>
<td>Low-pressure systems were located in the PRD region and Hainan province on September 28 and October 8. The weather was cloudy in the afternoon on these two days. On October 2 and 14, low-pressure systems (trough) were observed in northern and southern China. The temperatures and solar radiation levels were high on these two days, reaching daily maximum values of 24<del>27 °C and 775</del>886 W/m$^2$, respectively. The winds were mostly from the southeast at TW, those at TMS were from the east and northeast at low speeds. Rainfall was observed on the days of September 20-25, October 7, and 9-12.</td>
<td>The levels of O$_3$ and alkyl nitrates were low at TMS and TW on September 28 and October 2. Over the 4 sampling days, the maximum levels of O$_3$ and alkyl nitrates were observed on October 8, with O$_3$ (total alkyl nitrates) reaching peaks of 97 ppbv (125 pptv) at TMS and 65 ppbv (129 pptv) at TW.</td>
</tr>
<tr>
<td>October 18~19, 2010</td>
<td>The tropical cyclone Megi was formed in the South China Sea. The temperature and solar radiation started to decrease from October 18 to 19. The prevailing winds were from the north at TMS and changed from southeast to north from October 18 to 19 at TW.</td>
<td>The daily maximum levels of O$_3$ decreased from 95 ppbv on October 18 to 85 ppbv on October 19 at TMS. Diurnal patterns with maximum values in the afternoon were observed for alkyl nitrates at TMS and TW.</td>
</tr>
<tr>
<td>October 27~28, 2010</td>
<td>The tropical cyclone S.T. Chaba was located about 600 km east of Taiwan in the Philippine Sea and moving north. The winds at the two sites were mostly from the north. The temperature started to decrease, with daily maximum values reaching 16 and 25 °C at TMS and TW, respectively. Air pollutants started to accumulate. The maximum levels of O$_3$ reached 80 and 50 ppbv at TMS and TW, respectively. The levels of alkyl nitrates on these two days were lower than those on October 23 and 24, reaching maximum total levels of 95 and 94 pptv at TMS and TW, respectively.</td>
<td></td>
</tr>
<tr>
<td>November 20~21, 2010</td>
<td>On the south edge of the high-pressure system located in North China, the weather was sunny. Prevailing southeast winds were observed at TW. The prevailing winds at TMS were from the east. The solar radiation levels were low on November 20, reaching maximum values of 428 and 507 W/m$^2$ at TMS and TW, respectively. O$_3$ concentrations decreased to low levels at TMS and TW, with maximum hourly average values of 67 and 33 ppbv, respectively. The levels of alkyl nitrates decreased at the two sites on November 19. High alkyl nitrates mixing ratios were observed at midnight at TW.</td>
<td></td>
</tr>
</tbody>
</table>
Figure S1. Synoptic charts for the sampling days influenced by tropical cyclones (a) and anticyclones (b-d).