General Comments:

The revised manuscript by Ling et al. has improved greatly – the significant revisions have added substance to their analysis as well as improved the overall flow of the document. The principal points are now articulated more clearly, so the value of the measurements can be recognized. Additionally, the revised figures are now easier to assess and now strengthen the manuscript. However, I do feel that there still is a fair amount of editorial work to be done (word choice and sentence structure) on this version of the manuscript. Overall, the authors have done a good job responding to the comments and modifying the manuscript.

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.

Specific Comments:

Abstract:

P2L2-3: You should include “Mt. Tai Mo Shan” to introduce TMS and “Tsuen Wan” for TW

Reply: Thanks for the comment. “Mt. Tai Mo Shan” and “Tsuen Wan” have been added in the text. For details, please refer to Lines 2-3, Page 2 in the revised manuscript.

P2L4-8: Revise to something like:

Although the levels of parent hydrocarbons were much lower at TMS ($p<0.05$), similar alkyl nitrate levels were found at both sites regardless of the elevation difference, suggesting various source contributions of alkyl nitrates at the two sites, ~~which was proved by the analysis of photochemical evolution of alkyl nitrates~~.

Reply: Thanks a lot for the revision. The text has been revised accordingly. For details, please refer to Lines 4-7, Page 2 in the revised manuscript.

P2L23: NO is not “nitrous oxide” – change to nitric oxide

Reply: Thanks for the comment. “nitrous oxide” has been revised to “nitric oxide” in the text. For details, please refer to Line 22, Page 2 in the revised manuscript.

P2L25: This same point is addressed later, but in terms of ozone production, you should refer to it as this, ozone production – if the rates are negative, it means that ozone is being destroyed, but it’s still technically the “production rate”. Moreover, if it’s a “reduction rate”, a negative value (as in the abstract) would imply production (reads as a double negative), so be mindful of the language and sign convention.

Reply: The reviewer’s comment is highly appreciated. “-4.1 and -4.7” has been revised to “4.1 and 4.7” in the text. For details, please refer to Line 24, Page 2 in the revised manuscript.

P6L11-20: I suggest revising this paragraph – not clear as written.

Reply: Thanks for the comments. The paragraph has been revised as follows:
"The Tai O sampling station was a rural/coastal site ….. (Figure 1). This site overlooks the Pearl River Estuary to the west and north, and the South China Sea to the south. It is 32 km away from the urban center to the east and about the same distance from Macau/Zhuhai to the west. Major man-made sources in the region are located to the east, north and southwest. Local emissions are small because of a sparse population and light traffic. Due to Asian Monsoon circulation, this site is frequently affected by polluted continental air masses from the highly industrialized PRD region of mainland China in cold seasons."
For details, please refer to Lines 12-19, Page 6 in the revised manuscript.

P6L12-4: Revise to something like: Further to the east (32 km) are the urban areas and to the north (the entire NE to NW corridor) is the polluted PRD region.
Reply: Thanks for the comment. The text has been revised as suggested. For details, please refer to Lines 12-19, Page 6 in the revised manuscript.

P7L4: replace duration with period.
Reply: Replaced as suggested. For details, please refer to Line 4, Page 7 in the revised manuscript.

P8L2&4: Start sentences with "Ozone" and "Carbon monoxide"
Reply: The text has been revised as suggested. For details, please refer to Lines 2 and 4, Page 8 in the revised manuscript.

P8L7: "2s" should be "2σ"
Reply: Sorry for the typo. "2s" has been replaced by "2σ". For detail, please refer to Line 7, Page 8 in the revised manuscript.

P8L8: Delete space after "2-"
Reply: Thanks for the comment. The space after "2-" has been deleted. For detail, please refer to Line 8, Page 8 in the revised manuscript.

P8L10-19: Revise to something like the following: The O3 analyzer was calibrated by using a transfer standard (Thermo Environmental Instruments (TEI) 11 49PS), while the other analyzers were calibrated daily by analyzing scrubbed ambient air (TEI, Model 111) and a span gas mixture weekly with a NIST (National Institute of Standards and Technology) traceable standard which was diluted to representative mixing ratios using a dynamic calibrator (Environics, Inc., Model 6100). The standard (Scott-Marrin, Inc.) contained 156.5 ppmv CO (±2 %), 15.64 ppmv SO2 (±2 %), and 15.55 ppmv NO (±2 %). 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 1-minute data.
Reply: Thanks for the comment. The text has been revised as suggested. For details, please refer to Lines 10-19, Page 8 in the revised manuscript.

P9L10-13: Add commas:
DMS was a typical tracer for marine emissions, while Ox (i.e., O3 + NO2) was used as the tracer of secondary formation through photochemical reactions, including the formation of alkyl nitrates, because O3 shares a common photochemical source with alkyl nitrates (Simpson et al., 2006).

Reply: The reviewer's chariness is highly appreciated. Commas have been added as suggested. For details, please refer to Lines 11-12, Page 9 in the revised manuscript.

P9L14: what about ethane? (…methane, propane…); additionally, it's more common to report the branched isomer before the normal isomer – that is, i-/n-butanes

Reply: Thanks for the comment. Alkyl nitrates' precursors include ethane. The text has been revised as follows:

"In addition to the aforementioned species, alkyl nitrate precursors, including methane, ethane, propane and *i*-/*n*-butanes, were input into the model."

For details, please refer to Lines 14-15, Page 9 in the revised manuscript.

P9L16: Start a new paragraph; replace "Different" with "Various".

Reply: Thanks for the comment. A new paragraph was started. "Different" was replaced by "Various".

For detail, please refer to Line 17, Page 9 in the revised manuscript.

P9L16-29: While you have used PMF v3.0, there is a newer version (5.0) which includes two additional methods to estimate error. I'm just curious why you are not using the most recent version.

Reply: Thanks for the reviewer's comment. As a matter of fact, when the manuscript was being written, the 5.0 version of PMF model was not available. Though some new functions were added in the new version of PMF model, we think that the fundamental principle for categorizing factor profile and contribution matrices was the same (the "model overview" in the user guide of PMF 3.0, 4.1 and 5.0). To see the difference in factor profiles and contributions from different versions of PMF model, we indeed compared the results extracted from PMF 3.0 and PMF 4.1 (Lyu et al., 2015). No difference was found. Therefore, in this manuscript, we presented the source apportionment results from PMF 3.0.

It seems odd that you give only one linear correlation value for each study site (L19). The PMF model gives an R2 for each species (predicted vs. measured concentration). How did you calculate an average R2 and is that meaningful?

Reply: The reviewer's comment is highly appreciated. The average R^2 was the correlation between the predicted average concentrations and the measured average concentrations of each species input into the model. On the other hand, the R^2 of each species (predicted vs. measured concentration) extracted from the model was 0.64~0.94 at TW. Therefore, the text in the manuscript has been revised as follows:

"Secondly, the correlation between the predicted and measured concentration of each species was fairly good at TW (R^2=0.64~0.94) after the PMF implementation."

For details, please refer to Lines 19-21, Page 9 in the revised manuscript.

For L22-L23, could you clarify what you mean by the Q values being stable? They should be similar between runs, is this what is meant? Also, can you elaborate on comparing the Q values in the robust mode being approximately equal to the degrees of freedom - I was not able to find this in the Friend et al. manuscript. Also, it would be useful to report the Q/Qexp value for the model run - the value should be close to 1, indicating all data points were fit well.

Reply: The reviewer's comment is highly appreciated. Yes, "the Q values were stable" means that they were similar between runs. Actually, the Q/Qexp value was close to 1, within the ranges of 0.97-0.98 at TW.

As suggested by the previous study (Lau et al., 2010), the Q values could be close to the degrees of freedoms which can be estimated by "mn-p(m+n)"(p is the number of factors, m is the number of selected species, and n is the number of the samples). According to the above equation, the calculated Q values were about 2400 and 2200 for TMS and TW, respectively, while the estimated Q(robust) values from the PMF model were about 3000 (3000-3006) and 3200 (3190-3439) for TMS and TW, respectively.

Therefore, to avoid misunderstanding on the description of Q value, the text in the manuscript has been revised as follows:

"Fourthly, the ratios of Q(robust)/Q(true) were close to 1 for 4-factor solution, within the ranges of 0.97-0.98 at TW, higher than those of 3-factor and 5-factor solutions, indicating all data points were fit better in the 4-factor solution. "

For details, please refer to Lines 23-15, Page 9 in the revised manuscript.

Reference:

Lau, A. K.H., et al., 2010. Source apportionment of ambient volatile organic compounds in Hong Kong. Science of the Total Environment 408, 4138-4149.

While the number of factors is reasonable in the paper, it would be useful to show/comment on how the number of factors was chosen. The number of factors should be based on what's physically meaningful, but there is a quantitative metric as well. The overall Q/Qexp ratio will decrease as you increase factor number (because the residual decreases).

Reply: The valuable comment is appreciated. We have added the following description into the manuscript to show how the number of factors was chosen:

"Fourthly, the ratios of Q(robust)/Q(true) were close to 1 for 4-factor solution, within the ranges of 0.97-0.98 at TW, higher than those of 3-factor and 5-factor solutions, indicating all data points were fit better in the 4-factor solution. Indeed, the extracted source profiles from the 4-factor solution were the most reasonable."

For details, please refer to Lines 23-26, Page 9 in the revised manuscript.

P11-12: Figure 2 - the Russo et al. values should also be adjusted to be meaningfully comparable as they were on the old UCI calibration scale.

Reply: Thanks for the comment. The data from Russo et al. (2010) has been refreshed and Figure 2 has been revised accordingly. For details, please refer to Figure 2 in the revised manuscript.

P13 – would be useful to show the ozone distributions at both sites (even as SI) to enhance the discussion.

Reply: Thanks for the comment. The distributions of O_3 and other trace gases, as well as the time series of meteorological conditions at the two sites are presented in Figure S1. For details, please refer to Figure S1 in the supplementary information. A description of Figure S1 is provided in the text as follows:

"…while Figure S1 presents the time series of trace gases and meteorological parameters at the two sites."

For details, please refer to Line 30, Page 8 and Line 1, Page 9 in the revised manuscript.

P13L12: Replace "weather" with "meteorological"

Reply: Thanks for the comment. "weather" was replaced with "meteorological". For details, please refer to Line 17, Page 13 in the revised manuscript.

P13L15: Replace first "weather" with "meteorological" and delete the second "weather"

Reply: Thanks for the comment. The text has been revised as suggested. For details, please refer to Lines 20-21, Page 13 in the revised manuscript.

P14L10-11: Revise to: "…suggesting an important source of C3-C4 alkyl nitrates which was photo-oxidation of the parent hydrocarbons. For the C1-C2 alkyl nitrates, the temporal pattern…"

Reply: Thanks for the comment. The text has been revised as suggested. For details, please refer to Lines 12-14, Page 14 in the revised manuscript.

Additionally, "peaks and troughs" is used several times throughout the manuscript - I would recommend using more appropriate wording corresponding to the key point to made (i.e., max & min, temporal, etc.)

Reply: Revised as suggested. The description of "peak concentrations" and "trough" has been revised as "maximum concentrations" and "minimum concentrations", while the "peak values" and "troughs" have also been revised as the "maximum values" and "minimum values" as suggested.

For details, please refer to Lines 25 and 27, Page 13, Line 22, Page 14, Lines 20-21, Page 24, and Lines 9 & 11, Page 25 in the revised manuscript.

P15: Figure 4 – convert the NMHC mixing ratios to ppbv for clarity.

Reply: The units of NMHC mixing ratios in Figure 4 have been converted to ppbv. For detail, please refer to Figure 4 in the revised manuscript.

P15L10-13: Revise to something like: Although the levels of the parent hydrocarbons were lower at TMS, similar values of alkyl nitrates were observed at both sites, regardless of the elevation, suggesting the contributions of different sources and/or the influences of different air masses.
Reply: Thanks for the comment. The sentence has been revised as suggested. For details, please refer to Lines 11-13, Page 15 in the revised manuscript.

P16L1: Change "in-depth studied" to "analyzed".
Reply: The "in-depth studied" has been changed to "analyzed". For detail, please refer to Line 2, Page 16 in the revised manuscript.

P16L16: Change "destruction" to something like "removal"
Reply: Revised as suggested. For detail, please refer to Lines 12 & 16, Page 16 in the revised manuscript.

P17L20: Change "could be" with "were".
Reply: Revised as suggested. For details, please refer to Line 20, Page 17 in the revised manuscript.

P17L29: Change "laid" to "were positioned"
Reply: "laid" has been changed to "were positioned". For detail, please refer to Line 29, Page 17 and Line 1, Page 18 in the revised manuscript.

P19-20L20-3: Revise to something like the following:
For example, the average MeONO2 and EtONO2 mixing ratios at Hok Tsui, a PRD regional background site, were 10.4 ± 0.7 and 9.6 ± 0.7 pptv (unpublished data, 2001-2002), respectively.
Reply: Thanks for the comment. The sentence has been revised. For details, please refer to Lines 20-2, Pages 19-20.

P21L15-23:
Revise to something like the following: The average yields of 1- and 2-PrONO2 were 0.032 ± 0.004 and 0.22 ± 0.02, respectively, higher than the laboratory kinetic values by factors of 4—9 (Kwok and Atkinson, 1995). This confirms the presence of additional emissions of C3 alkyl nitrates at TW, including locally-emitted C3 alkyl nitrates and/or secondary formation other than the production pathway from propane to proxyl radical and PrONO2 (Reeves et al., 2007; Worton et al., 2010). The slope of 1-PrONO2 to 2-PrONO2 at TW was 0.15 (R2 = 0.80, $p < 0.05$), lower than the theoretical ratio of 0.21, further demonstrating the influence of other significant sources on ambient mixing ratios of C3 alkyl nitrates at TW.
Reply: Thanks for the comment. The sentences have been revised as suggested. For details, please refer to Lines 14-22, Page 21 in the revised manuscript.

P21L29-30: What do you mean by the signatures were damaged?"…the source signatures of alkyl nitrates and their parent hydrocarbons were damaged at this mountain site."

Reply: Sorry for the misunderstanding. The description has been revised as follows: "Since the air masses arriving at TMS were photochemically aged (Guo et al., 2013a), the original source profiles of alkyl nitrates and their parent hydrocarbons were altered at this mountain site."

For details, please refer to Lines 26-29, Page 21 in the revised manuscript.

P23L11: Change to: "By summing up the mass of the alkyl nitrates in each source category,"

Reply: The text has been revised as suggested. For detail, please refer to Line 10, Page 23 in the revised manuscript.

P23L11&15: You aren't reporting "concentrations" here, these are mixing ratios or mole fractions. Especially for line 15, you say "absolute concentration" – this is a mole fraction/mixing ratio – concentration would be in molecules/cm^3.

Reply: Thanks for pointing this out. "Concentration" has been revised as "mixing ratio" in the manuscript. For details, please refer to Lines 11 and 14, Pages 23 in the revised manuscript.

P23L23: Delete "On the other hand", and say "For the…"

Reply: It has been revised as suggested. For detail, please refer to Line 22, Page 23 in the revised manuscript.

P23L28: What are "stronger" photochemical reactions?

Reply: Sorry for the inappropriate expression. The text has been revised as follows: "…higher degree of photochemical reactions".

For details, please refer to Line 27, Page 23 in the revised manuscript.

P24 – Figure 9 – not absolute concentration – what is presented is the summed mixing ratio.

Reply: Sorry for the mistake. It has been revised as "summed mixing ratio". For detail, please refer to Figure 9 in the revised manuscript.

P24L14-20: Is the point that you are trying to make that local sources are also influencing the mesoscale transport?

Reply: Thanks for the comment. The point we are trying to make was that biomass burning in the "meso" scenario was mainly related to local sources. Therefore, the sentence has been revised as follows:

"The contribution of biomass burning in the "meso" scenario was likely attributable to local emissions, including the cooking/heating activities in the small villages nearby…."

For detail, please refer to Lines 13-15, Page 24 in the revised manuscript.

Also – peaks and troughs: do you mean max and min?

Reply: Yes. It has revised as maximum values and minimum values, respectively. For details, please refer to Lines 20-21, Page 24 in the revised manuscript.

P24L22: add “for biomass burning” after “1 pptv”

Reply: Added. For detail, please refer to Line 22, Page 24 in the revised manuscript.

P25L2: add “emissions were” after “biomass burning”

Reply: Thanks for the comment. “emissions was” has been added in the text. For detail, please refer to Line 2, Page 25 in the revised manuscript.

P25L5: Change “(data not shown here)” to “(not shown)”

Reply: It has been revised as suggested. For detail, please refer to Line 5, Page 25 in the revised manuscript.

P26L11: Change to: “Except for MeONO2,”

Reply: It has been revised as suggested. For detail, please refer to Line 11, page 26 in the revised manuscript.

P26L22: What do you mean by “gradually undertaken”? Revise accordingly

Reply: Thanks for the comment. The text has been revised as follows:

“…was occurring, and …..”.

For detail, please refer to Line 22, Page 26 in the revised manuscript.

P26L23: add “levels of” after ambient

Reply: Added as suggested. For detail, please refer to Line 23, Page 26 in the revised manuscript.

P26L24-27: Revise this sentence. What do you mean by “the air masses flew down the mountain”?

Reply: Thanks for the comment. The text has been revised as follows:

“On the other hand, the night-time downslope flow occurred due to the mountain breeze after sunset until the next morning…….”

For details, please refer to Lines 24-26, Page 26 in the revised manuscript.

P26L30-31: should read: “…when the valley breeze occurred.”

Reply: Revised as suggested. For detail, please refer to Line 31, Page 26 in the revised manuscript.

P27L4: end the sentence after respectively; revise the following three lines.

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

“…during the same period, respectively. The results demonstrated that when there was mesocale circulation, the levels of alkyl nitrates at TMS were dominated by the photo-oxidation of their parenet hydrocarbons originated from the urban site TW, one

possible reason leading to similar levels of alkyl nitrates at the two sites, though the values of their parent hydrocarbons were lower at TMS."
For details, please refer to Lines 4-8, Page 27 in the revised manuscript.

P27L17: Delete "Indeed"
Reply: "Indeed" has been deleted in the text. For detail, please refer to Line 17, Page 27 in the revised manuscript.

P27L19: Delete "firmly" and change "confirmed" to "corroborated"
Reply: The text has been revised as suggested. For details, please refer to Line 19, Page 27 in the revised manuscript.

P27L20-21: Change to something like the following:
By excluding the locally-formed alkyl nitrates from their overall levels, the contribution of regional sources to alkyl nitrates was determined for TMS.
Reply: The sentence has been revised as suggested. For details, please refer to Lines 20-21, Page 27 in the revised manuscript.

P27L25-27: Change to something like the following:
It is noteworthy that the regional alkyl nitrates included influences from all source categories (photochemical, biomass burning and oceanic) in the inland PRD region.
Reply: Thanks for the comment. The sentence has been revised as suggested. For details, please refer to Lines 24-27, Page 27 in the revised manuscript.

P28L8: Change "of help to evaluate" to "useful for evaluating"
Reply: It has been revised as suggested. For detail, please refer to Line 8, Page 28 in the revised manuscript.

P28L12: Explain what is meant by "recover the loss of O3 due to the NO titration."? Revise accordingly.
Reply: The sentence has been revised as follows:
"In this study, the "oxidant" O_x (O_3 + NO_2) was considered to be a better representation of O_3 levels as it takes into account the effect of O_3 titration by NO."
For details, please refer to Lines 11-13, Page 28 in the revised manuscript.

P28L23: Delete "It was obvious that"
Reply: The words were deleted. For detail, please refer to Line 24, Page 28 in the revised manuscript.

P29L3: Again, as stated previously, a negative ozone reduction rate would imply production. I would refer to this as the ozone production rate, with a negative value meaning that there is ozone loss, or have it be an ozone loss rate, with the value being positive.
Reply: The reviewer's comment is highly appreciated. The "-4.1 and -4.7" has been

revised as “4.1 and 4.7”.
For details, please refer to Line 4, Page 29 in the revised manuscript.

P29L11: Delete “i.e.,”

Reply: Thanks. It has been deleted. For detail, please refer to Line 11, Page 29 in the revised manuscript.

P29L13: simulation should be plural (simulations)

Reply: Thanks. It has been revised. For detail, please refer to Line 13, Page 29 in the revised manuscript.

P30L10: “remarkable” is not an appropriate word choice, please revise.

Reply: Thanks for the comment. “remarkable” has been revised to “significant”. For detail, please refer to Line 10, Page 30 in the revised manuscript.

P30L14-18: Reads awkwardly – please revise

Reply: Thanks for the comment. The sentences were revised as follows:
“At TMS, photo-oxidation of the parent hydrocarbons from TW contributed 52-85% to the ambient levels of alkyl nitrates on the days with mesoscale circulations between the two sites. On the other hand, alkyl nitrates from the inland PRD region were responsible for 58-82% of the observed values at TMS on the days with regional influence.”
For details, please refer to Lines 14-18, Page 30 in the revised manuscript.

P30L22: Yet again, change to ozone production rate or ozone loss rate with the appropriate sign convention.

Reply: Thanks for the comment. The text has been revised as follows:
“….with a reduction rate of 4.1 and 4.7 pptv …”
For detail, please refer to Line 22, Page 30 in the revised manuscript.

P30L23-26: Change to something such as the following:
The findings of this study will aid in understanding the source contributions and photochemical formation pathways of alkyl nitrates in Hong Kong’s mountainous areas.

Reply: Many thanks for the suggestion. The sentence has been revised accordingly. For detail, please refer to Lines 23-25, Page 30 in the revised manuscript.

At last, we would like to express our sincere thanks to the reviewer for his/her 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

C_1-C_4 alkyl nitrates ($RONO_2$) were measured concurrently at a mountain site, *i.e.*, Mt. Tai Mo Shan (TMS), and an urban site, *i.e.*, Tsuen Wan (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 the elevation difference, suggesting various source contributions of alkyl nitrates at the two sites. Prior to using a positive matrix factorization (PMF) model, the data at TW were divided into "meso" and "non-meso" scenarios for the investigation of source apportionments with the influence of mesoscale circulation and regional transport, respectively. Secondary formation was the prominent contributor of alkyl nitrates in the "meso" scenario (60 ± 2%, 60.2 ± 1.2 pptv), followed by biomass burning and oceanic emissions, while biomass burning and secondary formation made comparable contributions to alkyl nitrates in the "non-meso" scenario, highlighting the strong emissions of biomass burning in the inland Pearl River Delta (PRD) region. 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 nitric 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.

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):

$RH + OH\cdot \rightarrow R\cdot + H_2O$, k_1, α_1 (R1)

$R\cdot + O_2 \rightarrow RO_2$; k_2 (R2)

$RO_2\cdot + NO \rightarrow RO\cdot + NO_2$, k_3, $1\text{-}\alpha_2$, (R3)

$RO_2\cdot + NO \rightarrow RONO_2$, k_4, α_2, (R4)

$RO + NO_2 \rightarrow RONO_2$, k_5 (R5)

where k_1, k_2, k_3, k_4 and k_5 are reaction rate constants. α_1 and α_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):

$RONO_2 + h\nu \rightarrow RO\cdot + NO_2$, J_{RONO2}, (R6)

$RONO_2 + OH\cdot \rightarrow$ 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 (Clemitshaw et al., 1997; Talukdar et al., 1997). Dry deposition has recently been recognized as another pathway for the removal of atmospheric alkyl nitrates (Russo et al., 2010; Wu et al., 2011).

Despite increased concern over photochemical pollution in Hong Kong and the greater Pearl River Delta (PRD) region, limited studies have focused on the characteristics of alkyl nitrates, which share a common mechanism with photochemical 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 ($CH_3O\cdot$) 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 + NO_2 → $RONO_2$ became important for $MeONO_2$ formation at 10 ppb NO_2 and dominant at 35 ppb NO_2. 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 C_1-C_4 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). This site overlooks the Pearl River Estuary to the west and north, and the South China Sea to the south. It is 32 km away from the urban center to the east and about the same distance from Macau/Zhuhai to the west. Major man-made sources in the region are located to the east, north and southwest. Local emissions are small because of a sparse population and light traffic. Due to Asian Monsoon circulation, this site is frequently affected by polluted continental air masses from the highly industrialized PRD region of mainland China in cold seasons. A detailed description of the site is provided in Wang et al. (2003).

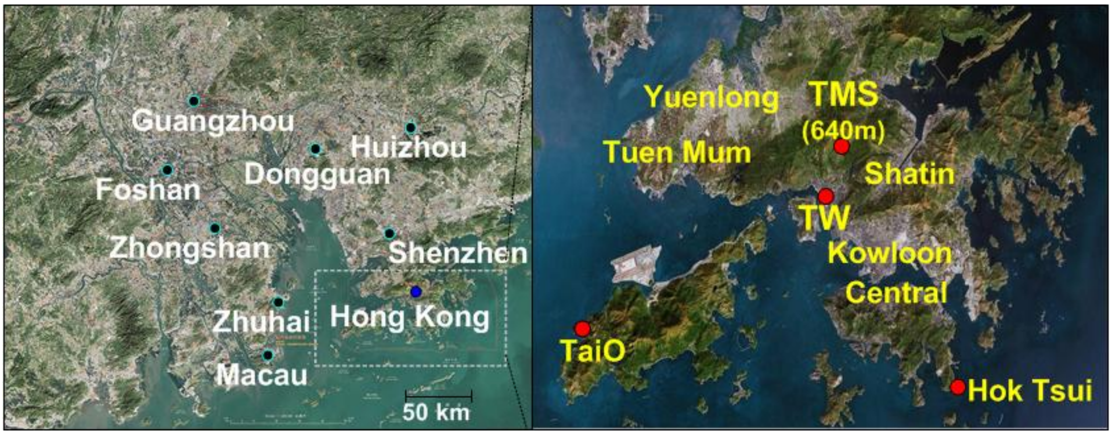

Figure 1. Tai Mo Shan (TMS) and Tsuen Wan (TW) sampling sites and the surrounding environments in Hong Kong.

2.2. Sampling and analysis of volatile organic compounds (VOCs)

Whole air samples were collected on 10 O_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 period. A total of 384 samples were collected at the two sites. The O_3 episode days were selected as the days with the highest daytime hourly O_3 level at a regional scale (higher than 100 ppbv), which were based on weather forecasts and meteorological data analysis, and confirmed by the observed O_3 mixing ratios. 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). After the campaign, the canister samples were sent to the University of California, Irvine (UCI) for chemical analysis. Other studies have provided detailed descriptions of the analytical system and the quality control, detection limits and analysis precision of the VOC samples (Simpson et al., 2006, 2010). In brief, the precision and detection limit of the alkyl nitrate measurements is 5% and 0.02 pptv, respectively. The calibration scale for the alkyl nitrate measurements changed in 2008, increasing by factors of 2.13, 1.81, 1.24 and 1.17 for the C_1, C_2, C_3 and C_4 alkyl nitrates, respectively (Simpson et al., 2011). In other words, the alkyl nitrates reported at Tai O by Simpson et al. (2006) were lower than the data reported here, and the Tai O data have been adjusted to the new calibration scale to allow direct comparison with this work. The Tai O sampling campaign was conducted from 24 August 2001 to 31 December 2002. Different from the air samples collected at TMS and TW, each whole-air sample at Tai O was collected for only 1-min, and was then analyzed at UCI. Intensive sampling from 0700-1900 LT was conducted every 2-h during the selected pollution episodes (17-19 October 2001, 29-30 August, 5-6 September, 9-11 and 25 October, 6-8 and 12 November 2002). Apart from the intensive sampling days, samples were taken either daily or every few days, typically in the midafternoon (Simpson et al., 2006).

2.3. Continuous measurements of O_3, CO and NO-NO_2-NO_x

At TMS, online measurements of O_3, CO and NO-NO_2-NO_x were made using commercial analyzers. Ozone was measured using a commercial UV photometric instrument (Advanced Pollution Instrumentation (API), model 400E) that has a detection limit of 0.6 ppbv. Carbon monoxide was measured with a gas filter correlation, nondispersive infrared analyzer (API, Model 300E) with a heated catalytic scrubber (as purchased) to convert CO to carbon dioxide (CO_2) for baseline determination. The detection limit was 30 ppbv for a 2-min average. The 2σ precision was about 1% for a level of 500 ppbv (2-min average) and the overall uncertainty was estimated to be 10%. NO, NO_2 and NO_x were detected with a chemiluminescence NO-NO_2-NO_x analyzer (API, Model 200E) that had a detection limit of 0.5 ppbv. The O_3 analyzer was calibrated by using a transfer standard (Thermo Environmental Instruments (TEI) 49PS), while the other analyzers were calibrated daily by analyzing scrubbed ambient air (TEI, Model 111) and a span gas mixture weekly with a NIST (National Institute of Standards and Technology) traceable standard which was diluted to representative mixing ratios using a dynamic calibrator (Environics, Inc., Model 6100). The Standard (Scott-Marrin, Inc.) contained 156.5 ppmv CO (±2%), 15.64 ppmv SO_2 (±2%), and 15.55 ppmv NO (±2%). For the O_3, CO, NO and NO_x analyzers, a data logger (Environmental Systems Corporation Model 8816) was used to control the calibrations and to collect 1-minute data.

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

At TW, hourly O_3, CO, NO–NO_2–NO_x and meteorological data were obtained from the HKEPD (http://epic.epd.gov.hk/ca/uid/airdata). The hourly data were derived by averaging 1-min data subsequently over the same time interval as the TMS data. Detailed information about the measurements, quality assurance and control protocols can be found in the HKEPD report (HKEPD, 2012). In addition, Table S1 in the supplementary information shows descriptive statistics of main non-methane hydrocarbons (NMHCs) and trace gases at both sites, while Figure S1 presents the time series of trace gases and meteorological parameters at the two sites.

2.4. Positive Matrix Factorization (PMF) model

In this study, the US EPA PMF 3.0 (http://www.epa/heasd/products/pmf/pmf.html) was used for the source apportionments of the observed alkyl nitrates at TW. Our previous studies provided detailed information about the PMF model (Ling et al., 2011; Ling and Guo, 2014). In terms of the PMF input, the uncertainty for each species was determined as the sum of 10% of the VOC concentration and two times the method detection limit (MDL) of the species (Paatero, 2000). Tracers for different sources were selected for the model input. For example, CO, ethane and ethyne were the tracers of combustion processes, and CH_3Cl 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, ethane, propane and *i-/n-*butanes, were input into the model. In total, sixteen compounds were used for the model input.

Various checks and sensitivity tests were conducted to examine the model performance. Firstly, many different starting seeds were tested and no multiple solutions were found. Secondly, the correlation between the predicted and measured concentration of each species was fairly good at TW (R^2=0.64~0.94) after the PMF implementation. Thirdly, the scale residuals, which are the uncertainty over the different runs for the input species, ranged between –3 and 3 for the PMF solution. Fourthly, the ratios of Q(robust)/Q(true) were close to 1 for 4-factor solution, within the ranges of 0.97-0.98 at TW, higher than those of 3-factor and 5-factor solutions, indicating all data points were fit better in the 4-factor solution. Indeed, the extracted source profiles from the 4-factor solution were the most reasonable. All the factors were mapped to a base factor in all the 100 runs in the bootstrapped simulation for the four-factor solution, suggesting the solution was stable. Lastly, the G-space plot extracted from the F-peak model results did not present oblique edges, reflecting that there was little rotation for the selected solution. Overall, the above features demonstrated that PMF provided reasonable results for the source apportionment of alky nitrates (Ling et al., 2011; Ling and Guo, 2014).

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

A photochemical box model coupled with Master Chemical Mechanism (PBM-MCM) was used to simulate the in-situ formation of alkyl nitrates at TMS and TW. The PBM-MCM was developed by assuming that it was a well-mixed box without the treatment of vertical or horizontal dispersion, and the air pollutants in the model were homogeneous. For the mechanism coupled in the model, the MCM (version 3.2) used in this study is a state-of-the-art chemical mechanism, which describes the degradation of 143 primary VOCs including methane and contains around 16,500 reactions involving 5900 chemical species (Jenkin et al., 1997, 2003; Saunders et al., 2003). The measured data, including O_3, CO, NO_x, SO_2, 54 VOCs and methane, together with the actual meteorological conditions of temperature, relative humidity and boundary layer in the region, were used to constrain the model. The photolysis rates of different species in the model were parameterized as suggested by the previous study (Pinho et al., 2009) using the photon flux determined from the Tropospheric Ultraviolet and Visible Radiation (v5) model based on the actual conditions, such as meteorological conditions, location and time period of the field campaign in Hong Kong (Lam et al., 2013). The model output simulated in-situ formation of alkyl nitrates and other secondary products as well as the full set of precursors, radicals and intermediates. To provide robust results from the model simulation, several measures were adopted for the model development. The detailed information for the model frameworks, the model development and the evaluation for the model performance has been reported in our previous studies (Lam et al., 2013; Ling et al., 2014).

3. Results and discussion

3.1 Descriptive statistics of alkyl nitrates and their parent hydrocarbons

Table 1 presents the descriptive statistics of alkyl nitrates and their parent hydrocarbons at TMS and TW. Figure 2 compares the levels of alkyl nitrates measured at TMS and TW with those measured in different environments in previous studies. In general, 2-PrONO_2 and 2-BuONO_2 were the most abundant alkyl nitrates at the two sites, consistent with the results observed in different environments (Blake et al., 2003; Simpson et al., 2006; Russo et al., 2010; Wang et al., 2013). The relatively higher levels of 2-PrONO_2 and 2-BuONO_2 were 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_2, EtONO_2 and 2-PrONO_2 were slightly higher at TW than at TMS ($p < 0.05$), with average values of 12.6 ± 0.5 (mean ± 95% confidence interval), 13.3 ± 0.6 and 26.3 ± 1.2 pptv, respectively, at TW. The average mixing ratios of 1-PrONO_2 and 2-BuONO_2 were comparable at the two sites ($p > 0.05$). The results were contradictory to the fact that the mixing ratios of their parent hydrocarbons at TMS were much lower than at TW, highlighting the complexity of sources of alkyl nitrates at both sites.

In comparison with other studies, the average mixing ratios of alkyl nitrates at TMS were much higher than those measured in forested areas in coastal New England (Russo et al., 2010) and in tropospheric air influenced by Asian outflow during the airborne TRACE-P mission (Simpson et al., 2003), where the levels of parent hydrocarbons were also lower. (Note that all of the UCI data shown in Figure 2 were adjusted to UCI's post-2008 alkyl nitrates' calibration scale to enable direct comparison (Simpson et al., 2011). However, the mean mixing ratios of C_1-C_3 alkyl nitrates were slightly lower and the 2-BuONO_2 mixing ratio was higher at TMS than at Tai O (Table 2), Hok Tsui and in Karachi, Pakistan (Barletta et al., 2002; the Karachi data have also been adjusted to the new UCI alkyl nitrates' calibration scale). The differences among TMS, Tai O and Hok Tsui might result not only from the levels of their parent hydrocarbons, but also from the influence of air masses with different photochemical ages and sources (Wang et al., 2003). Furthermore, as mentioned in Section 2.2, the sampling method and sampling period at TMS were different from those at Tai O and Hok Tsui, where the sampling duration was only 1-min and the sampling time varied on different sampling days. In particular, many whole air samples were collected during O_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.

Species	TMS			TW		
	Mean*	Min.	Max.	Mean	Min.	Max.
$MeONO_2$	10.9±0.4	6.2	21.4	12.6±0.5	7.2	26.6
$EtONO_2$	12.1±0.5	3.2	25.6	13.3±0.6	4.0	35.0
2-$PrONO_2$	24.1±1.1	4.0	51.2	26.3±1.2	6.0	49.2
1-$PrONO_2$	3.8±0.2	0.4	10.6	4.0±0.2	0.7	8.1
2-$BuONO_2$	32.0±1.7	3.1	80.1	34.2±1.9	5.1	92.8
Methane (ppmv)	2.0±0.1	1.8	2.2	2.0±0.1	1.8	2.5
Ethane	1908±78	396	3588	2224±90	717	4315
Propane	1101±75	106	4455	3551±415	1443	33800
n-Butane	830±91	97	6252	4486±482	1372	34700

* Average ± 95% confidence interval

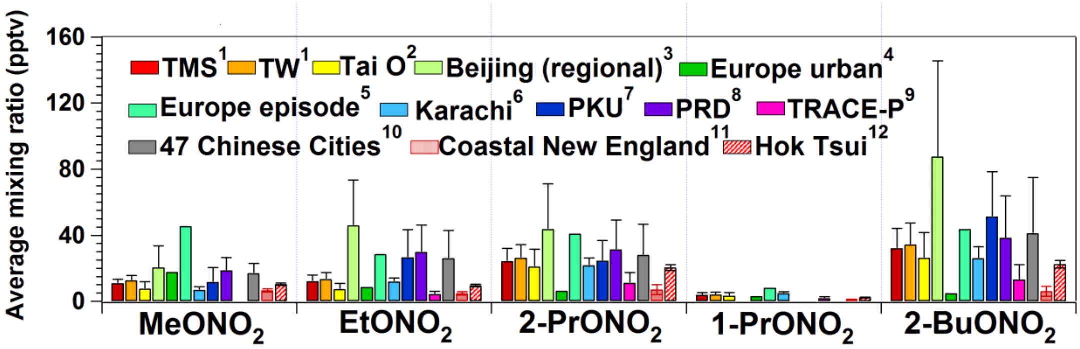

Figure 2. Comparison of alkyl nitrate mixing ratios in different locations. Data collected by UCI before 2008 (PRD and TRACE-P) were adjusted to UCI's new calibration scale to permit direct comparison (see text for details about the new calibration.

[1.] This study, September-November, 2010. [2.] Rural site, August 2001-December 2002 (Simpson et al., 2006). [3] Urban site, 2009-2011 (Wang et al., 2013). [4] Urban sites, April-May 2004 (Worton et a., 2010). [5] Urban sites, April-May 2004 (Worton et al., 2010). [6] Coastal site, December 1998-January1999 (Barletta et al., 2002). [7] Urban site, August-September 2011 and December 2011-January 2012 (Wang et al., 2013). [8] Regional background sites, September 2009 (Wang et al., 2013). [9] Aircraft measurement, February-April 2001 (Simpson et al., 2003). [10] Urban sites, July 2009 (Wang et al., 2013). [11] Coastal site, January-February and June-August 2002, July-August 2004 (Russo et al., 2010). [12] Regional background site, March 2001-April 2002 (unpublished data).

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).

Compound	Minimum	Maximum	Median	Mean
$MeONO_2$	5.5	52.2	13.4	15.9
$EtONO_2$	2.7	34.3	12.1	13.1
1-$PrONO_2$	0.2	14.5	3.5	3.9
2-$PrONO_2$	2.4	65.9	24.5	32.6
2-$BuONO_2$	0.8	89.8	27.4	30.7
Methane (ppmv)	1.75	3.70	1.96	2.05
Ethane (ppbv)	0.38	5.05	2.14	2.12
Propane (ppbv)	0.006	13.0	1.54	2.05
n-Butane (ppbv)	0.006	12.8	0.95	1.64

Table S2 and Figure S2 in the supplementary information summarize the synoptic weather conditions and the corresponding variations of O_3 and alkyl nitrates on O_3 episode and non-O_3 episode days at both sites. In general, meteorological conditions including temperatures, winds and solar radiation significantly influenced the levels of air pollutants (Table S2). High mixing ratios of O_3 and alkyl nitrates were usually associated with meteorological conditions with high-pressure system and/or stable conditions, such as high temperatures, intense solar radiation and low wind speeds. Figure 3 shows the time series of C_1-C_4 alkyl nitrates on O_3 episode and non-O_3 episode days at both sites, while Figure 4 presents the temporal variations of their parent hydrocarbons accordingly. Although the ranges of alkyl nitrate mixing ratios were similar and maximum values were observed in the afternoon, the day-to-day variations of individual alkyl nitrates differed during the sampling period at both sites. The maximum values were comparable and the diurnal patterns well tracked each other for C_3-C_4 alkyl nitrates at TMS and TW, especially on the days (24 October to 3 November, 9 and 19 November) with relatively higher O_3 mixing ratios ($p < 0.05$). The average daytime O_3 mixing ratios (0700-1800) on the high O_3 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-O_3 episode days. Typically, the average daytime levels of 2-$PrONO_2$, 1-$PrONO_2$ and 2-$BuONO_2$ on high-level O_3 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-O_3 episode days ($p < 0.05$), implying that secondary formation of alkyl nitrates might be more prominent on O_3 episode days. Coincident with the high C_3-C_4 alkyl nitrates during high O_3 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 the parent hydrocarbons. For the C_1-C_2 alkyl nitrates, the temporal patterns of $MeONO_2$ and $EtONO_2$ were different at the two sites, especially on high-level O_3 days. The peaks of $MeONO_2$ and $EtONO_2$ 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 C_1-C_2 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 maximum 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).

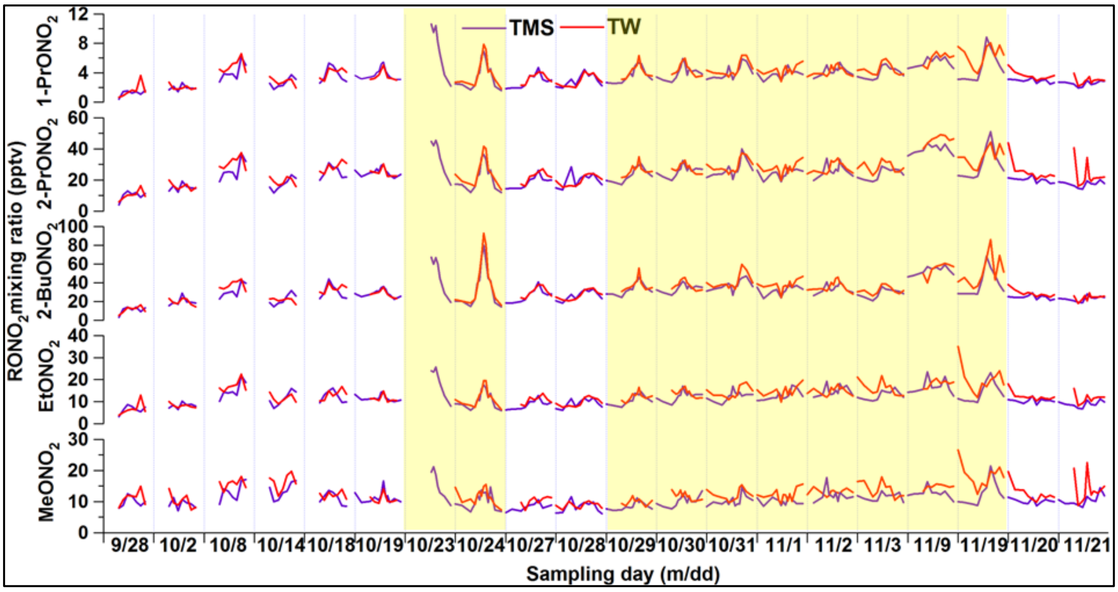

Figure 3. Time series of $MeONO_2$, $EtONO_2$, $1\text{-}PrONO_2$, $2\text{-}PrONO_2$ and $2\text{-}BuONO_2$ measured at TMS (purple) and TW (red) in 2010. The yellow shading highlights the O_3 episode days.

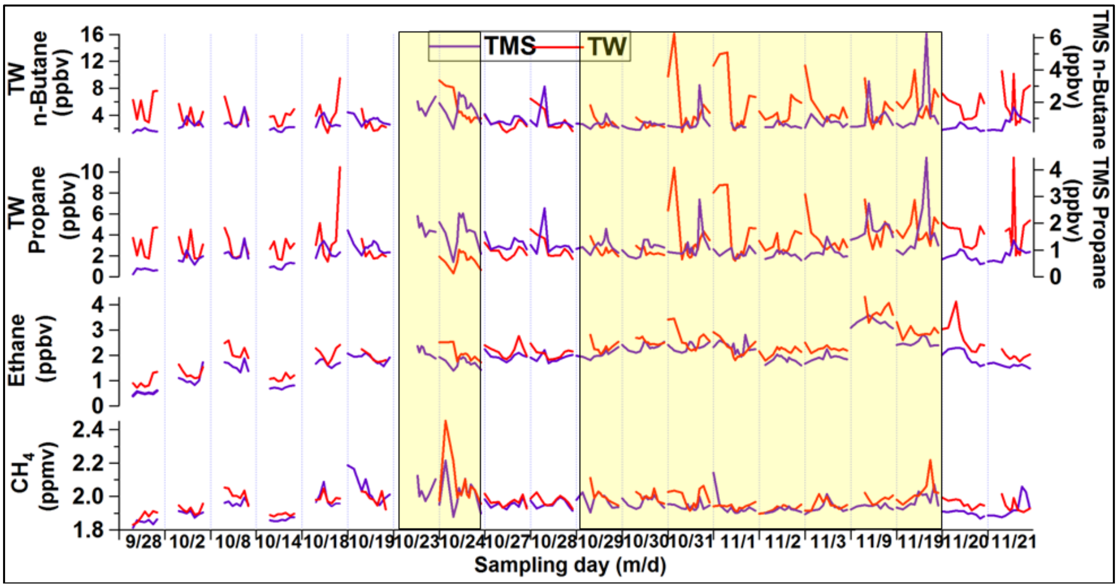

Figure 4. Time series of the parent hydrocarbons of alkyl nitrates at TMS and TW. The yellow shading highlights the O_3 episode days.

Although the levels of the parent hydrocarbons were lower at TMS, similar values of alkyl nitrates were observed at both sites, regardless of the elevation, suggesting the contributions of different sources and/or the influences of different air masses. Hence, the source apportionments of alkyl nitrates, contributions of reaction pathways for the secondary formation of alkyl nitrates, and the relationship between O_3 and alkyl nitrates were analyzed in the following sections.

3.2. Sources of alkyl nitrates

3.2.1. Photochemical evoluation 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 NO_x-rich, making the reaction with NO being the dominant pathway for the removal of RO_2 radicals (Russo et al., 2010). In this study, the average mixing ratios of NO_x at TMS and TW were 10.7 ± 0.3 and 56.3 ± 1.6 ppbv, respectively, indicating that the environment was NO_x-rich (> 0.1 ppbv, Roberts et al., 1998). Hence, reaction with NO was the main pathway for the removal of RO_2 radicals at the two sites. In addition, the results of PBM-MCM model simulation confirmed that the hydrogen abstraction reaction from the parent hydrocarbon, namely the reaction of hydrocarbon with OH radical, was indeed the rate-limiting step for photochemical production of alkyl nitrates at both sites (Lyu et al., 2015).

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

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):

$$\frac{RONO_2}{RH} = \frac{\beta k_A}{k_B - k_A}\left(1 - e^{(k_A - k_B)t}\right) \quad (2)$$

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 anlysis 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, α_1, α_2 and J_{RONO2} were 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 were positioned above their PP curves at shorter processing time ($t < 1$ d) and converged towards the PP curves at longer processing times ($t = 1.5$-2 d) (Figure 5), resulting from the decreased influence of the parameter $\frac{[RONO_2]_0}{[RH]_0} e^{(k_A - k_B)t}$ 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 $[RONO_2]_0/[RH]_0$ 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 intial ratio. Similarly, Figure 6 shows the relationships of C_1-C_3 $RONO_2/RH$ to 2-$BuONO_2$/*n*-butane at TW.

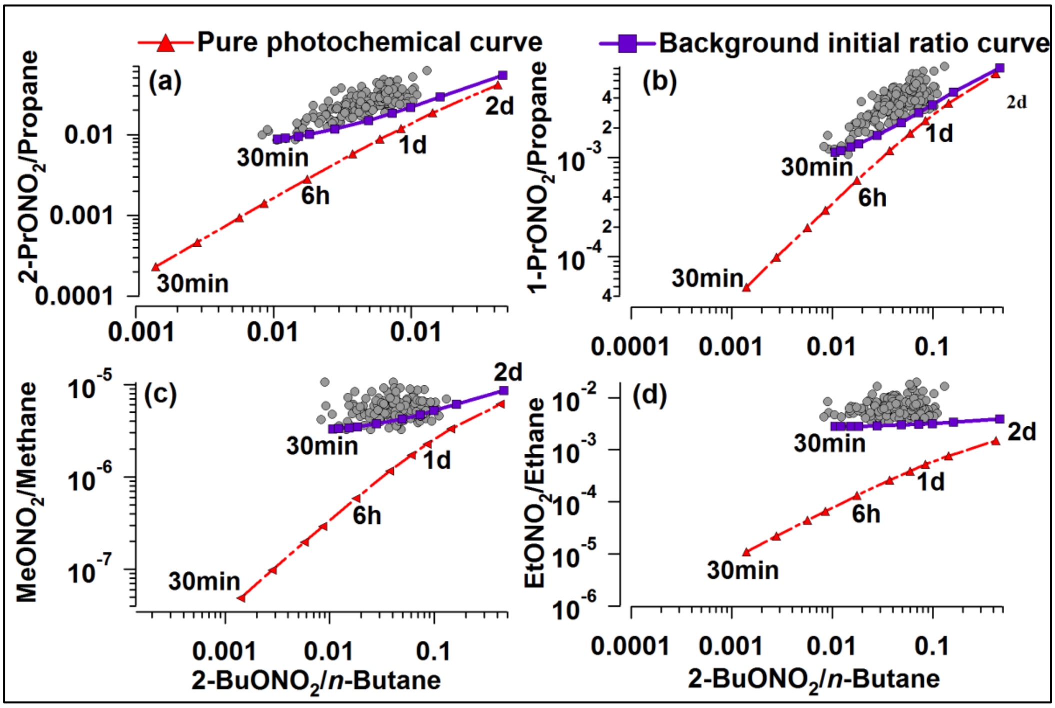

Figure 5. Relationships of C_1-C_3 $RONO_2/RH$ with 2-$BuONO_2$/*n*-butane at TMS. The red dashed curves were obtained based on zero initial concentrations of RH and alkyl nitrates (pure photochemical curves, PP), while the blue solid curves were obtained based on non-zero initial levels (background initial ratio curves, BIR), with the lowest ratios of $RONO_2/RH$ from 0000 to 0700 LT.

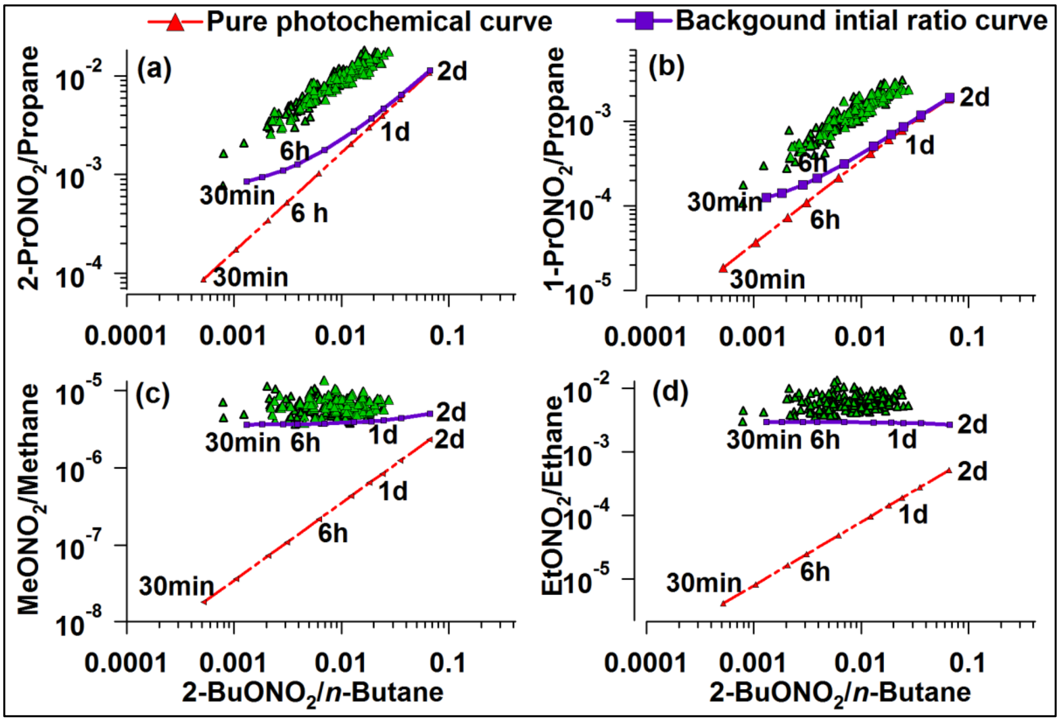

Figure 6. Relationships of C_1-C_3 $RONO_2$/RH with 2-$BuONO_2$/*n*-butane at TW. The red dashed curves were obtained based on zero initial concentrations of RH and alkyl nitrates (pure photochemical curves, PP), while the blue solid curves were obtained based on non-zero initial levels (background initial ratio curves, BIR), with the lowest ratios of $RONO_2$/RH from 0000 to 0700 LT.

At TMS, the measured ratios of $MeONO_2$/methane and $EtONO_2$/ethane to 2-$BuONO_2$/*n*-butane were much higher than the ratios in the PP curves (Figure 5c & d), with the observed ratios larger than their theoretical ratios by factors of 5-25. As expected, the observed trends approached the PP curves at a longer processing time, suggesting that the measured ratios of C_1-C_2 $RONO_2$/RH to 2-$BuONO_2$/*n*-butane were influenced by aged air masses 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 $RONO_2$/RH to 2-$BuONO_2$/*n*-butane in BIR curves was comparatively smaller, further confirming that there were other sources contributing to ambient C_1-C_2 alkyl nitrates besides photochemical formation, including the background levels of C_1-C_2 alkyl nitrates and their parent hydrocarbons (direct measurements of RH in Table 1) (Wang et al., 2013). For example, the average $MeONO_2$ and $EtONO_2$ mixing ratios at Hok Tsui, a PRD regional background site, were 10.4 ± 0.7 and 9.6 ± 0.7 pptv (unpublished data, 2001-2002), respectively.

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 different from those in the PP and BIR curves (Russo et al., 2010; Wang et al., 2013). For example, the slopes of the observed ratios of 1- and 2-$PrONO_2$/propane to 2-$BuONO_2$/*n*-butane were 0.04 ± 0.01 and 0.26 ± 0.02, respectively, while the slopes for the BIR curves were 0.02 ± 0.01 (PP curve: 0.02 ± 0.01) and 0.12 ± 0.01 (0.10 ± 0.01), respectively. This was reasonable 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 backround 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 $\beta_{1\text{-PrONO2}}/\beta_{2\text{-PrONO2}}$ (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

C_3 alkyl nitrates.

At TW, the comparison between the observed ratios of C_1-C_2 $RONO_2/RH$ to 2-$BuONO_2$/*n*-butane and the ratios from the PP and BIR curves was consistent with that at TMS. However, in terms of C_3 alkyl nitrates, although the evolution of the measured ratios of C_3 $RONO_2/RH$ to 2-$BuONO_2$/*n*-butane followed the trends of the ratios in the PP and BIR curves, the measured ratios of C_3 $RONO_2/RH$ to 2-$BuONO_2$/*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 C_3 alkyl nitrates (Wang et al., 2013) (details in Section 3.2.2). High emissions of propane provided sufficient precursors of C_3 alkyl nitrates, and the lifetimes of 1-$PrONO_2$ and 2-$PrONO_2$ were long enough to sustain relatively high levels at TW. To further investigate the influence of additional sources on the distributions of C_3 alkyl nitrates at TW, equation 1 was used to fit the measured ratios of 1- and 2-$PrONO_2$/propane to calculate the yield of C_3 alkyl nitrates (β). The average yields of 1- and 2-$PrONO_2$ were 0.032 ± 0.004 and 0.22 ± 0.02, respectively, higher than the laboratory kinetic values by factors of 4–9 (Kwok and Atkinson, 1995). This confirms the presence of additional emissions of C_3 alkyl nitrates at TW, including locally-emitted C_3 alkyl nitrates and/or secondary formation other than the production pathway from propane to proxyl radical and $PrONO_2$ (Reeves et al., 2007; Worton et al., 2010). The slope of 1-$PrONO_2$ to 2-$PrONO_2$ at TW was 0.15 (R^2 = 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 C_3 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 original source profiles of alkyl nitrates and their parent hydrocarbons were altered at this mountain site. Therefore, only the data collected at the urban site were used for source apportionments of alkyl nitrates.

High concentrations of O_x and alkyl nitrates were found in the first factor at both sites, implying that this factor was associated with secondary formation. In addition, certain amounts of combustion species, such as ethane, ethyne, propane, *n*/*i*-butanes, benzene and CO were present in this factor. It is not surprising that O_x correlated with the aforementioned species given that O_3 is a secondary pollutant formed from photochemical oxidation of RH (Ling and Guo, 2014). The second factor was distinguished by a significant presence of methyl chloride, ethene, ethyne and benzene along with certain amounts of methane, propane and *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.

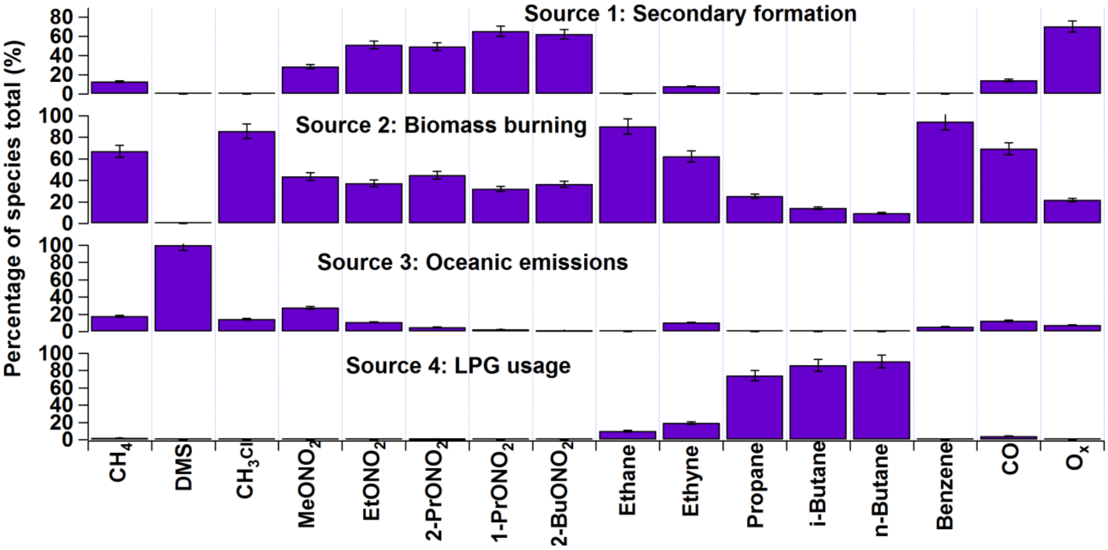

Figure 7. Explained variations of species in the identified sources extracted by the PMF model for TW.

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.

By summing up the mass of the alkyl nitrates in each source category, the overall mixing ratios in each source were obtained and the contribution of each individual source to alkyl nitrates at both sites was calculated. Figures 8 and 9 present the source contributions to individual alkyl nitrates for the "meso" and "non-meso" scenarios in percentage and in mixing ratio at TW, respectively. The mixing ratios of total alkyl nitrates (*i.e.*, $\Sigma\ RONO_2=MeONO_2 + EtONO_2 + 1\text{-}PrONO_2 + 2\text{-}PrONO_2 + 2\text{-}BuONO_2$) 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). For the "non-meso" scenario, the contributions of biomass burning (46 ± 2% or 34.2 ± 0.7 pptv) and secondary formation (44 ± 2% or 32.9 ± 0.7 pptv) were comparable, and the oceanic emissions contributed 10 ± 1% or 7.0 ± 0.07 pptv to the total alkyl nitrates. The higher contribution of secondary formation in the "meso" scenario at TW was mainly due to higher degree of 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.

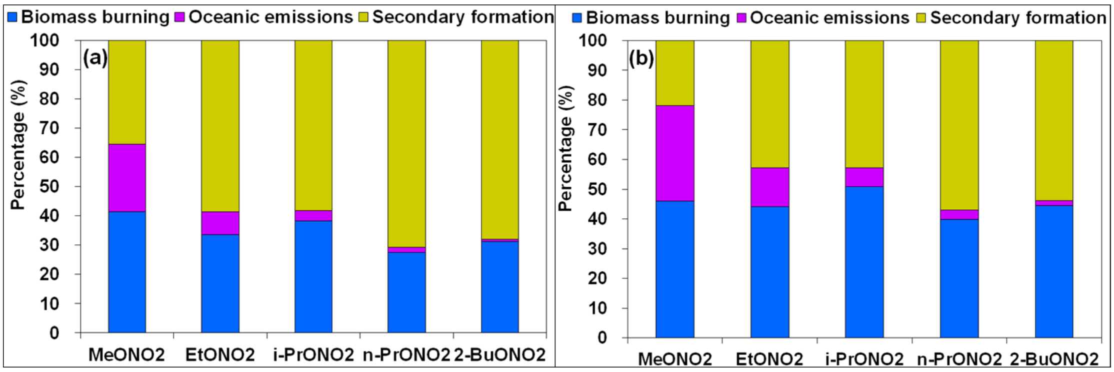

Figure 8. Source contributions to individual alkyl nitrates in (a) “meso” and (b) “non-meso” scenarios at TW (in percentage).

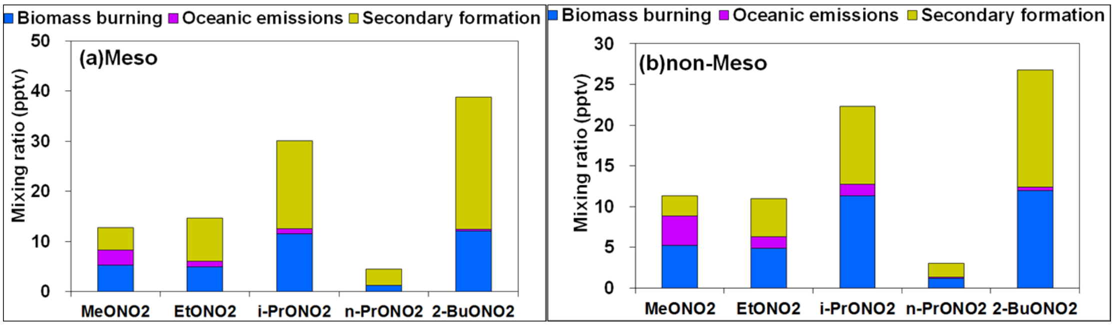

Figure 9. Source contributions to individual alkyl nitrates in (a) “meso” and (b) “non-meso” scenarios at TW (in summed mixing ratio).

In addition, although the percentage contribution of biomass burning was higher in the “non-meso” scenario, the absolute mixing ratios of biomass burning were comparable in the two scenarios. Figure 10 shows the diurnal patterns of ΣRONO$_2$ from biomass burning and oceanic emissions in “meso” and “non-meso” scenarios at TW. The contribution of biomass burning in the “meso” scenario was likely attributable to local emissions, including the cooking/heating activities in the small villages nearby and the frequent barbecue activities at the 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 maximum values were not statistically different from the minimum values. The difference of the average mixing ratio of ΣRONO$_2$ between daytime and nighttime hours was only 1 pptv for biomass burning. The weak diurnal variations in the “non-meso” scenario suggests that the contribution of fresh biomass burning emissions was insignificant, revealing the influence of regional transport from the PRD region. This speculation was confirmed by the analysis of 12-h backward trajectories, which showed that air masses in the “non-meso” scenario were mainly from the inland PRD region (not shown). It is noteworthy that although air masses were more aged in the “non-meso” scenario, the levels of alkyl nitrates were comparable to those in the “meso” scenario, highlighting the strong emissions of biomass burning in the PRD region (Yuan et al., 2010).

For the oceanic emissions, a minimum mixing ratio during daytime hours was found for $\sum RONO_2$ in the “meso” scenario, while a broad peak was present during daytime hours in the “non-meso” scenario. The daytime minimum mixing ratio in the “meso” scenario at TW was related to uplifted valley breezes that brought alkyl nitrates away from TW to TMS, while the higher nighttime values were probably 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.

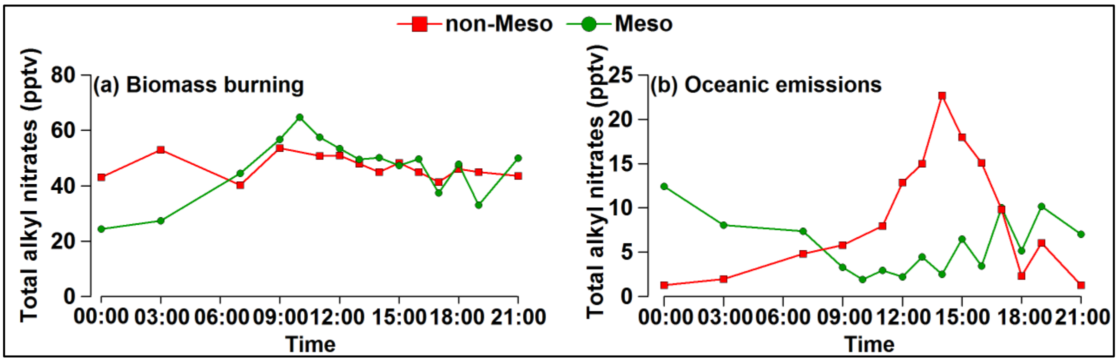

Figure 10. Diurnal patterns of (a) biomass burning and (b) oceanic emissions for “meso” and “non-meso” scenarios at TW.

Moreover, the contributions of oceanic emissions to C_1-C_2 alkyl nitrates were higher than C_3-C_4 alkyl nitrates, with average percentages of 23% and 32% for the “meso” and “non-meso” scenarios (Figures 8 and 9), suggesting the importance of oceanic emissions to C_1-C_2 alkyl nitrates, consistent with the results of previous work

(Simpson et al., 2003). Instead, the C_3-C_4 alkyl nitrates were dominated by the secondary formation in the "meso" scenario (58-71%), while the contributions of biomass burning and secondary formation to C_3-C_4 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). Except for $MeONO_2$, which had comparable levels in both "meso" and "non-meso" scenarios, the mixing ratios of daytime C_2-C_4 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 $EtONO_2$, *i*-$PrONO_2$, *n*-$PrONO_2$ and 2-$BuONO_2$, respectively. To quantify the influence of mesoscale circulation on the mixing ratios of alkyl nitrates at TMS, a moving box model coupled with master chemical mechanism (Mbox) was applied to the data collected on the days influenced by mesoscale circulation (*i.e*, "meso" scenario) (Guo et al., 2013a). The model was developed based on an idealized trajectory movement between TMS and TW sites, with air pollutants transported from TW to TMS through the valley breeze during daytime hours (0800-1700 LT) when photochemical formation of alkyl nitrates was occurring, and eventually contributed to the ambient levels of alkyl nitrates at TMS. As such, the model was only constrained with the observed daytime data at TW. On the other hand, the night-time downslope flow occurred 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 C_1-C_4 alkyl nitrates simulated by the Mbox model at TMS, *i.e.*, the values under the "meso" scenario. It should be noted that the comparison was only made for daytime alkyl nitrates (0800-1700LT), when the valley breeze occurred. The average mixing ratios of $MeONO_2$, $EtONO_2$, 1-PrONO$_2$, 2-PrONO$_2$ and 2-ButONO$_2$ at daytime hours estimated using the Mbox model were 9.97 ±0.85, 7.38 ±0.44, 3.08 ±0.16, 18.7 ±0.77 and 34.7 ±3.14 pptv, respectively, accounting for 86%, 52%, 66%, 65% and 86% of the observed values at TMS during the same period, respectively. The results demonstrated that when there was mesocale circulation, the levels of alkyl nitrates at TMS were dominated by the photo-oxidation of their parenet hydrocarbons originated from the urban site TW, one possible reason leading to similar levels of alkyl nitrates at the two sites, though the values of their parent hydrocarbons were lower at TMS.

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

Scenario	$MeONO_2$	$EtONO_2$	1-$PrONO_2$	2-$PrONO_2$	2-$BuONO_2$
"Meso"	9.97 ± 0.85	7.38 ± 0.44	3.08 ± 0.16	18.7 ± 0.77	34.7 ± 3.14
In-situ formation	3.61 ± 0.48	2.18 ± 0.29	1.03 ± 0.13	3.68 ± 0.45	10.9 ± 1.31
Regional transport	7.07 ± 0.50	8.44 ± 0.62	2.11 ± 0.22	16.86 ± 1.17	15.15 ± 1.49

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 useful for evaluating 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 "oxidant" O_x ($O_3 + NO_2$) was considered to be a better representation of O_3 levels as it takes into account the effect of O_3 titration by NO. 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). 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 O_3 reduction and the photochemically formed alkyl nitrates at TMS ($R^2 = 0.42$) and TW ($R^2 = 0.72$), with the average O_3 reduction rate of 4.1 and 4.7 pptv/pptv, respectively. Namely, O_3 was reduced by 4.1 and 4.7 pptv if 1 pptv of alkyl nitrates were formed at TMS and TW, respectively.

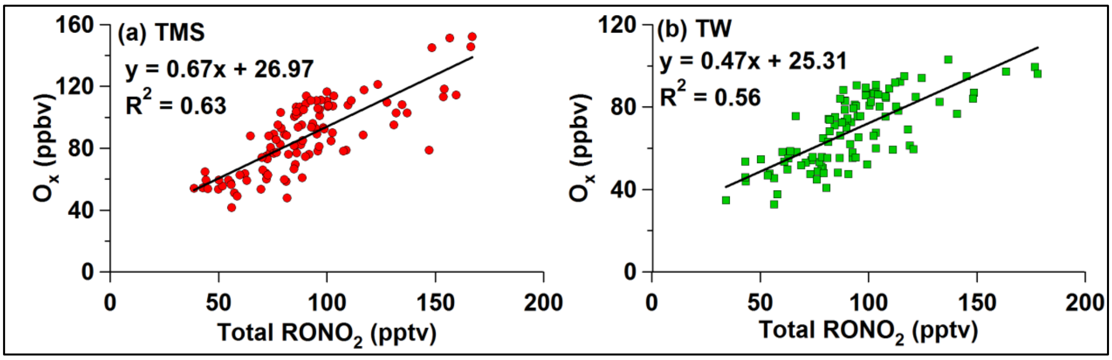

Figure 11. Correlation between O_x ($O_3 + NO_2$) and total alkyl nitrates at (a) TMS and (b) TW.

Moreover, because secondary alkyl nitrates are formed through two main reaction pathways, “$RO_2 + NO$” and “$RO + NO_2$”, it is of interest to investigate the relative contribution of the above pathways to the formation of alkyl nitrates. Two scenarios for model simulations were run and compared. The first scenario was the base case in which the model was run with all reaction pathways opened, while the second scenario was the constrained case in which the pathway of $RO_2 + NO \rightarrow RONO_2$ was shut down. It was found that the reaction of “$RO_2 + NO$” was the prominent pathway for the secondary formation of alkyl nitrates at the two sites. The contributions of $CH_3O_2 + NO$ to $MeONO_2$ accounted for about 72% and 50% of the secondarily formed $MeONO_2$, while the contributions of $RO_2 + NO$ were 97-99 and 95-99% of the secondarily formed C_2-C_4 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 $RO_2 + NO$ to $MeONO_2$ at the two sites were related to the higher levels of CH_3O from the oxidation of CH_4 and the decomposition of larger RO_2 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 significant impact on the levels of alkyl nitrates at the two sites. At TW, secondary formation was the dominant contributor to alkyl nitrates when there was mesoscale circulation, while the contributions of secondary formation and biomass burning were comparable under the influence of regional transport. At TMS, photo-oxidation of the parent hydrocarbons from TW contributed 52-85% to the ambient levels of alkyl nitrates on the days with mesoscale circulations between the two sites. On the other hand, alkyl nitrates from the inland PRD region were responsible for 58-82% of the observed values at TMS on the days with regional influence. The photo-oxidation of parent hydrocarbons from TW and regional transport 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 will aid in understanding the source contributions and photochemical formation pathways of alkyl nitrates in Hong Kong's mountainous areas.

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