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Atmospheric Chemistry and Physics Discussions

Interactive comment on "New insight into the spatiotemporal variability and source apportionments of C_1–C_4 alkyl nitrates in Hong Kong" *by* Z. H. Ling et al.

Anonymous Referee #2

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General Comments:

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.

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 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 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.

In its current form, I do not feel that 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 logical 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.

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.

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.

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.

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

P5, L24: "The natural territory. . ." again, inappropriate terminology – I think you mean "The natural landscape".

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 temper-

ature was higher and the relative humidity and wind speed were lower at TW (Guo et al., 2013a)."

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.

P6, L16-25: "Sixty-minute integrated VOC samples. . ." reads awkwardly, revise to something like the following: "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 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)."

Revise the following: ". . .which were forecasted based on weather parameters and meteorological data analysis, and subsequently confirmed by the observed O3 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 O3 mixing

ratios."

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.

P6, L27: "the VOC samples were delivered to UCI. . ." should be "the canister samples were sent to UCI. . ."

P7, L5: ". . .the C2, C2, C2 and C2 RONO2, respectively" All of the subscripts are C2s – please correct.

P7,L10-13: Change to: At TMS, trace gases measurements of O3, CO and NO-NO2-NOx were made using commercial analyzers. . ."

What is "regular internal calibration"? Please elaborate.

P7, L20: Change to: "For the O3, CO, NO and NOx analyzers,. . ."

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. . ."

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.

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 gasses 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.

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.

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.

P9, L21: "forest" should be "forested"

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 alkyl 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 alkyl nitrates everywhere. . .we already know this, the key is to hone in on the factors driving the spatial distributions at you sampling locations.

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.

P11, L9-10: change to “. . .peak values were observed in the afternoon,. . .”

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?

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).”

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.

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.”

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

P12, L10-13: Regarding MeONO2, what about the coastal and marine influences? This should at least be mentioned.

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.”

P13, L6: What does “The increment of RONO2” mean? Consider revising.

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.

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

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).

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

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.

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]0eˆ(kA-kB)t on the difference between the two curves as the photochemical age increased (Wang et al., 2013).

P15, L8-10: Revise to something like: "This feature was more pronounced for C3 RONO2 at TW (Fig. 5*) because of the lower values of [RONO2]0=[RH]0 resulting

from the high mixing ratios of propane at that site (Ling et al., 2014)."

Isn't this also the case for the 2-butyl nitrate and n-butane?

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

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.

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.

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?

P17, L12: "brought to TMS" should be "transported to TMS"

Section 3.2.4 – change/add the figure numbers accordingly

In addition to the ratios of RONO2/RH and the photochemical age of air masses, a comparison of the measured ratios of C1–C3 RONO2/RH to 2-BuONO2/n-butane and PP and BIR curves could provide useful information about the evolution of RONO2 at the two sites (Fig. 5*).

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

P18, L6-8: Revise as follows: "Our previous field measurements at Hok Tsui, a PRD regional background site, had average MeONO2 and EtONO2 mixing ratios of 4.9+/-0.3 and 5.3+/-0.4 pptv (unpublished data, date?), respectively."

You do not need to say that you have confirmed the existence of background levels of ambient RONO2 – this is already demonstrated by the minimum/lowest quartile/percentile values at your sites.

P18, L29: "analyzed" should be "examined"

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.

P20, L16: "Figure 6" should actually be "Figure 7"

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?

P22, L16: Confirming the existence of background levels of RONO2 and RH at both sites is not a conclusion – please omit.

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?

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.

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 22597, 2015.