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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Long term O_3-precursor relationships in Hong Kong: Field observation and model simulation" *by* Yu Wang et al.

Anonymous Referee #2

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The authors report an analysis of time series for O3, NOx, TVOCs and CO for Hong Kong for the years 2005-2014. Based on a seasonal analysis of observed and modeled data using an observation-based box model coupled with CB05 mechanism the authors find different trends of these pollutants for each season. Overall, they state that locally produced O3 increased in spring and decreased in autumn over the years. The authors suggest that different decreasing rates in O3 precursors NOx and TVOC as well as changes in VOC composition and/or VOC reactivity (mainly caused by decrease of aromatic compounds) might have led to these O3 trends. For the autumn season the authors state that regional O3 might have been a dominant factor in the O3 trend. An analysis of incremental reactivity showed decreasing contribution from aromatic compounds, while the contribution from alkenes appeared to increase over the years. This might have been due to changing VOC source contributions (less solvents, more

traffic emissions). Overall, this paper shows some valuable material and associated discussion. However, there are some important issues which need to be addressed before this paper can be accepted.

Major issues:

1) In most figures intra- and inter-annual variations are significantly larger than the 2005-2014 trend. For instance, the O3 trend shows the highest increase from 2005-2014 (0.67 ppb/yr) in autumn (Fig. 3). However, this trend is only determined by 3 "outlier" months of the years 2012, 2013, 2014. These 3 months are just 10% of this specific data set. Another example is Fig. 5 which shows very large scatter in O3 data for the autumn season. Also, for instance Fig. S10 about the annual trends of VOC/NOx ratios is largely determined by the last two years. The question is: how robust are all the trends shown in this paper?

2) According to HKEPD (2015) long-term trends for O3, NOx, and CO may have been different within the Hong Kong area and not necessarily the same as at the TC site. For O3, annual values at the rural site were highest, but did not change that much over the years, while urban and New Town sites show some increase at overall lower levels than at the rural site. Apart from that NOx values did not change that much for New Town sites, while urban sites indeed showed some slight decrease. For CO there were actually some increases at urban sites over the last years in contrast to New Town sites. The question is: how representative is the TC site for a trend analysis for Hong Kong?

3) I think the most interesting results are shown in Figs 6 and 7. Fig 6 shows that Ox has remained unchanged over the last years. This is basically in line with the trends shown in HKEPD (2015), i.e. some slight decrease of NO2 compensated by some slight increase of O3. Actually, the authors' statement on page 16 L6-18 could be a valid reason for changes in ambient O3 as it has been shown that NO2/NOx ratios may have increased due to a changing traffic fleet (e.g. Carslaw, 2005; Rappengluck et al.,

2013). I recommend that the authors elaborate on this, as it may be the larger fraction of directly emitted NO2 which may cause an increase in O3, even at overall decreasing NOx mixing ratios. I was wondering, whether Fig 7 shows day- and nighttime data? An enhanced traffic related NO2/NOx ratio would be better discernable at night excluding secondarily produced NO2 at daytime.

4) Fig. 3 shows some interesting feature. Not only all O3 precursor values are lowest in summer, but also O3 values in summer are lower than in spring and lower than in autumn. They are just slightly higher than in winter. This is a bit astonishing as one would expect highest O3 values in summer. I was wondering whether the authors can shed some light on this and explain the specific summertime conditions.

Other comments:

Page 4 L5-8: The reference HKEPD (2015) lists various instruments being used in the Hong Kong network. What instruments were actually installed at TC, what were their detection limits, what their resolutions? Was NO2 measured directly?

Page 4 L9: I am surprised to see that only 21 VOCs were identified and quantified at TC given the fact that it is an urban site. Looking into the CO data, which varies between 400 ppb and more than 1 ppm as monthly means (Fig 2), I would expect significantly higher number of VOCs. I doubt the authors can consider the sum of the quantified VOCs as the total VOCs (TVOCs). What do the authors estimate is the fraction of the quantified VOCs on the entire mass of VOCs in ambient air at TC?

Page 4 L13-14: How was the accuracy of 1-7% determined?

Page 5 L25-29: The authors only measured 21 VOCs. What assumptions did the authors have on other VOCs not measured, but needed as an input for MCM?

Page 5 L30-31. It sounds like MCM has been developed by the authors referenced in this sentence. This should be clarified.

Page 6 L2-4: The way the authors describe I can hardly understand the difference

between "background" and "baseline" values. While the definition of "baseline values" is literally taken from the reference TF HTAP (2010) the term "background values" the authors use is different from what is defined in TF HTAP (2010).

Page 6, L16-18: How were these VOC lifetimes based on: on reactions with OH, O3, NO3, Cl? What were the concentration assumptions on these species? Did the authors consider that the VOC lifetimes might be different during the course of the day, in particular at night?

Page 6 L19: Meteorological conditions could be something like windspeed, humidity, temperature, radiation, something which is actually not unique to NO2....What meteorological conditions do the authors exactly mean?

Page 6 L18-20: What reaction exactly shows exponential relationship with temperature?

Page 6 L21: Do these lifetimes for NO2 include all NO2 relevant reactions or do they refer to just one specific reaction? Please explain why uncertainties show up in these lifetimes. Why were those lifetimes calculated for each season, but not for each day, as the model is run for each day?

Page 6 L25: Where do the uncertainties in the wind speed calculations come from?

Page 7 L7-8: Please explain how O3 will be produced with titration by NO.

Page 7, L16: With regard to the precursors NOx, total VOCs and CO did the authors calculate arithmetic means or medians? Would there be differences?

Page 7 L19-20: Please explain whether the monthly maximum O3 level was the monthly averaged daily maximum 8-h O3 average or something else?

Page 8 L6: It sounds like toluene was reduced in LPG. Please verify, if this was meant, as usually most significant toluene emission sources are solvent and traffic exhaust related emissions. What about other aromatics apart from toluene?

Page 8 L8-10: Given the fact that TVOCs almost remained unchanged it is not that much surprising to see O3 increases in VOC limited areas. It would be different in NOX limited regimes.

Page 8 L9: It sounds like the references cited here were the first to find that urban areas in general are VOC limited. Please verify whether this is true or whether this statement refers to recent findings in Chinese cities only.

Page 12 L11: I was just wondering if the definition of daytime (0700-1900 LT) is valid regardless what season is concerned.

Page 12 L15-16: While this statement is true for the modeled data, the observations show a completely different result.

Page 12 L28: "...who attributed the increasing O3 trend ....to local contribution and regional transport". Isn't this statement always and at any given site true?

Page 12 L31-32: "..(0.70$\pm$0.34 ppbv/yr and 0.66$\pm$0.41 ppbv/yr)"... I do not see any of these values in Fig 4.

Page 12 L33-34: I am astonished to read that the model did not consider the influence of solar radiation. Isn't this a crucial parameter which has not been considered?

Page 13 L1: What is the reason for the increase in solar radiation over the last years?

Page 13 L2-3: What is the quantitative contribution of the increase in solar radiation for in-situ photochemical reactivity of VOCs?

Page 13 L6-7: What are the contributions quantitatively?

Page 18, L16-17: Fig 8a shows highest RIR from TVOC and CO, while NOx has the least negative RIR. Wouldn't this mean that O3 production would be most efficient in winter, which would be in contradiction to observed O3 values in winter (Fig. 3)?

Page 19, L3-6: It looks like RIR values for BVOC (here only isoprene) in summer are

higher than those for the remaining AVOCs for the same season. Would this mean that summertime O3 production critically depends on biogenic emissions in Hong Kong in summer.

Page 19, L6-7: "The higher RIR of BVOCs in summer was due to the higher photochemical reactivity". Wouldn't it be higher biogenic emissions which cause higher BVOC RIR in summer?

Page 19, L8-10: NOx RIR is less low in winter compared to spring and summer. Wouldn't this already lead to higher O3 production in winter according to the authors?

Page 19, L21: Is this statement valid for entire Hong Kong or just for the TC site?

Page 20, L9-10, Fig. 9: The trend analysis in Fig 9 is mostly driven by a few strong peaks. How robust is this analysis? Looking into the different y-scales of Fig. 9 I conclude that summertime O3mixing ratios are largely due to the high BVOC levels, which would be in line with Fig. 8. Again, is Hong Kong's O3 pollution mostly caused by BVOCs?

Page 21, L17: "...increased emissions of alkenes from traffic related sources". Is this due to enhanced alkene emissions from changes in the composition of the traffic fleet or from increased traffic volume? If it is the latter, then emissions of aromatic compounds would also increase.

Page 21, L20-21: Diesel driven vehicles emit significantly less VOCs than gasoline driven vehicles. In other words was the DCV program a significant contribution to the overall traffic related alkene emissions?

Page 21, L26-28: Why would the AVOC (alkane) contribution to O3 formation not increase with increasing alkane levels in 2005-2013?

Page 21, L29-30: "In addition,...blur the trend". I do not understand this sentence. Also, what photolysis rates of alkanes do the authors exactly mean?

Page 21, L34: Here you should add the Reiman et al paper, as this was one of the first to observe anthropogenic isoprene emissions.

Page 22, L6-7: The authors state that 90% of isoprene was emitted from biogenic sources, while traffic sources were less than 5%. From what sources did the remaining 5% isoprene come from?

Figure 4: (1) There is no gold line (ΔO3) for summer. (2) the observations (blue line) is always the highest. What is the model missing?

Figure 8: Is this data day- or nighttime data or both and why did the authors choose that specific time period?

Figure S9: I am not sure about the units (M m-2) for Solar Radiation here.

Literature cited:

Carslaw D. (2005): Evidence of an increasing NO2/NOx emissions ratio from road traffic emissions, Atmos. Environ., 39, 4793-4802, 2005. Rappengluck et al. (2013): Radical Precursors and Related Species from Traffic as Observed and Modeled at an Urban Highway Junction, J. Air Waste Man. Assoc., 63:11, 1270-1286, doi: 10.1080/10962247.2013.822438 Reimann et al. (2000), The anthropogenic contribution to isoprene concentrations in a rural atmosphere, Atmos. Environ., 34(1), 109–115, doi:10.1016/S1352-2310(99)00285-X

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