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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Inter-comparison of O_3 formation and radical chemistry in the past decade at a suburban site in Hong Kong" *by* Xufei Liu et al.

Anonymous Referee #3

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The paper describes a monitoring study of trace gases at a suburban site close to the airport in Hong Kong. A comparison is made of ozone concentrations over a ten year period via detailed analysis of three periods, coupled with master chemical mechanism / box model calculations to facilitate interpretation. This analysis is coupled with a source apportionment analysis for VOCs and with discussion of policy changes in the area. The study is one of a sequence of detailed papers that have investigated air quality, and especially ozone production, in this area, especially in relation to air quality policy. This paper adds to that corpus of knowledge and understanding and should be published. The authors should consider the following points:

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1.The Introduction gives references to the large series of investigations of which this paper is the latest. It is important to understand what these papers have contributed to our understanding of air quality in Hong Kong, and information is provided, but it is quite difficult to appreciate fully. It would be helpful if a table was provided, listing the main contributions (not all need be included and there are some overlaps) of these papers: target pollutant, nature of the monitoring, main conclusions.

2.The main aim of the paper is to investigate the changes in ozone through measurement of the major inorganic species, including ozone, and a wide range of VOCs, at a single site. The observations are supported and interpreted using a box model based on the master chemical mechanism. There are several issues that warrant further discussion than they are given in the text, and some clarification:

i)The site (Tung Chung, TC) is close to a highway serving the airport which is only 3 km away. The mean NO and NO2 concentrations are not too high, but the maximum values are. It is commented that one reason for low [O3] could be titration by NO. An analysis of the degree of titration would be helpful.

ii)The paper is based on analysis of three periods covering 2007 – 2016. There can be significant year to year variations resulting, for example, from meteorological rather than AQ policies. Figure 2 shows that long term trends in hourly ozone at TC and shows that decreases have, on average, occurred since 2013. The figure is very difficult to interpret, though, since it shows log[O3]. The low concentrations, presumably at night, are of little interest. It would be much easier to understand what is happening if this plot were linear in [O3].

iii) Some further discussion of the locally produced and regionally transported ozone (p5 line 109) would be helpful. The wind speeds are generally quite low, so the distances the precursors and ozone itself are transported is not large. How significant is precursor transport? Are the sources greater in some directions for the longer-lived precursors? How significant is this? The assertion that the regionally transported emis-

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sions can be determined by difference as asserted on p5 needs some moderation – the chemistry isn't linear and the simulations aren't 100% accurate, as demonstrated by some apparently negative regional sources.

iv)HONO was not monitored in 2016 and the 2011 values were used. Some justification, based on measurements elsewhere, is provided. Figure 7 shows the OH formation and loss rates and demonstrates the importance of HONO in the early morning, especially in 2016. The potential error in this rate analysis should be emphasised.

v) This last point illustrates one of the deficiencies of the paper – the tendency to discuss the behaviour of average values and reaction rates rather than delve into the diurnal variations, which show some interesting effects, some difficult to understand. For example, in Fig 7, the high NO + HO2 rate shows that the chain length is quite long, especially in 2007 – the propagation rate considerably exceeds the initiation rates (mainly O3 + alkene and O1D + H2O). The OH production from HONO is largely balanced by HONO formation from OH + NO except in the early morning. On the other hand, the termination rate (OH + NO2) is quite large and significantly exceeds the initiation rates. Why is this? It needs some explanation. The effects are still there in the later years, although less pronounced.

vi) It would help understand these arguments, and those given on page 25, if Fig S3 were shown, and discussed in more detail, in the main text. Why do the concentrations of HO2 and RO2 increase in the late afternoon in 2016?

vii)The concentrations of oxygenates are very high (Table S4), yet their sources are not discussed in the main text. Are they produced by reaction or are there emission sources? Were the concentrations constrained, or were they simulated. Were high concentrations of other oxygenates generated in the simulations?

viii) Why were the BVOC concentrations so low in 2007 (Fig S4)? The temperature was slightly lower, but not by much, and the solar irradiance was higher (Table S5)

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ix)While the analysis of the impact on O3 of the emission changes, via the scenario B simulations, is of considerable value, it is important, once again, to point out that the chemistry is non-linear and the approach limits the quantitative, but not the qualitative, nature of the conclusions.

x) Small point: the decrease in [OH] of less than 10% between 2007 and 2013 could hardly be described as significant (p24, line 502)

Some of these comments require relatively detailed responses, which may need to be consigned to the Supplement to avoid over complication of the main text. It is important, though, that the issues related to the detailed chemistry are resolved since much of the emphasis of the paper depends on the box model calculations.

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