

Interactive comment on “Ozone production and hydrocarbon reactivity in Hong Kong, Southern China” by J. Zhang et al.

Anonymous Referee #3

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The manuscript analyzes measurements of ozone and its precursors in the Hong Kong region to show that anthropogenic VOCs, particularly aromatics, are dominating the VOC reactivity during 10 ozone episodes in autumn 2002. The authors capitalize upon distinct source signatures in mainland China vs. Hong Kong, as observed in the ratio of enhancements in CO to enhancements in NO_y, to classify the episodes according to the contribution of local (Hong Kong) vs. regional (transport from mainland China) precursor emissions. An observation-based model is applied to show that VOCs drive the ozone formation during these episodes, whereas high NO_x concentrations suppress ozone production. Finally, HONO is identified as an important early morning source of OH.

Understanding the ozone chemical production regime (NO_x-saturated vs. NO_x-limited)

is critical for identifying effective ozone reduction strategies, and this study thus provides information relevant for decreasing ozone in Hong Kong. The measurements presented here should also be useful for testing emission-based models of ozone formation in the Hong Kong region.

There are several sections where additional explanations would greatly strengthen the manuscript (for example, showing evidence for the transport classification in Section 3.1.3, and more fully presenting the uncertainty analysis on p. 8983). Overall, it is well-written and should be suitable for publication once the concerns outlined below have been addressed.

Specific comments:

It would be helpful to place ozone episodes in autumn in the context of other seasons; do the highest ozone concentrations typically occur in the fall in the Hong Kong region?

Section 2: In several places, the reader is referred to earlier work; a brief summary of the major findings would be helpful. For example, what do Zhang et al (2004) conclude about typical transport patterns at night vs. day (2.1) ? The discussion of previously studied longer-term trace gas data (2.2) might fit better in the introduction, with a summary of the main findings.

A description of the instruments used in this study should be included in the manuscript, perhaps in a Table where the instrument could be briefly described and referenced, and the sites & time periods for which it is operational could be listed (and the “VOC” column removed from table 1), along with measurement frequency, precision, and accuracy. The authors could then eliminate some of the text on p. 8966.

Section 3.1.1: Nov 8 is singled out as potentially different from the >100 ppb episode days, but I didn’t find any discussion later in the text as to whether the 100 ppb threshold signifies unique conditions.

p. 8969: The ozone concentrations are near zero on 25-Oct and 7-Nov where 3b

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shows high NO - these days could be pointed out to illustrate the occurrence of NO titration. The authors should provide evidence for the statement that ozone “peaks during the afternoon (as a result of photochemical production and to a less extent downward mixing of ozone from above the boundary layer)”. Also, some discussion could be added as to the relative roles of variations in mixing depths and transport patterns in contributing to the diurnal cycles shown in Figure 3.

I'd like to see the evidence for the results discussed in Section 3.1.3. Thresholds for a “high” vs. “low” ratio should be defined. Were there any consistent patterns in the timing of the “transient spikes of high ratios” across the days?

I find it surprising that CO reactivity is often higher than biogenics. What are “typical” isoprene and pinene concentrations vs. the AHCs at these sites? From the hourly measurements at TO, is it clear that the biogenics aren't ever important during the day? When is the seasonal peak of biogenic emissions in this region?

p.8974: Could a biogenic source explain the R-OLE contribution at TM?

What does reactivity look like on non-episode days?

p. 8977: Is there observational evidence that the VOCs contributing most to reactivity here are negligible above the boundary layer? Is the outflow from the mainland predominantly advected in the boundary layer?

Does the iterative modeling approach to determine the diurnal VOC profiles give substantially different results than simply assuming the shape of the observed diurnal profile at TO applies to the EPD sites? I'd like to see the diurnal profiles at all sites, but most important is to convince the reader that the approach works by showing observed vs modeled at TO. If the shape of the diurnal profiles are substantially different at the various sites, some explanation should be included.

p. 8981: Please explain the significance of the mixing-height-dependent rate constant. How do the results shown here (HONO more important than HCHO and other aldehy-

des as a source of HOx) compare to published studies in other cities/regions?

p.8982: Some additional explanation of a negative RIR would be helpful (e.g., titration/radical scavenging) Can you define a threshold for transitioning between NO_x-saturated and NO_x-sensitive for a given VOC reactivity? (I don't see why 5.5 ppb NO is "significantly lower" than 7.6 ppb.)

p. 8983 The sensitivity analysis should be expanded upon. I recommend giving details on the specific sensitivities examined, along with the results, perhaps in a Table. Is it correct to conclude that in future analyses, it would be appropriate to use available 24-hr average concentrations without creating hourly data to drive the OBM?

Technical corrections:

More precise, quantitative language could be used in several places through the text, e.g.: "light local emissions", "relatively new town" (p. 8965); "enough sensitivity" (p. 8967); "generally high" (p. 8968), "relatively early/late" (p. 8969)

A few paragraphs begin with incomplete phrases followed by a colon, that read as if they were intended to be titles (e.g. pp.8973; 8980; 8982)

The discussion of the OBM sensitivity calculations seems out of place in Section 2 and may fit better in the uncertainty analysis section at the end of the paper.

Bottom of p. 8969: CO is also high on some non-episode days.

Top of p. 8969: TUV does not seem to be particularly high on 7-Nov.

p. 8970 What are the "secondary pollutants" shown in Figure 3? What were the "unusual nighttime transport patterns"?

p. 8972: Typo (?) in the phrase, "since its extremely low reactivity through its high concentration"

p. 8979: How exactly is the "observed O₃ increment" estimated? The discussion of

“agreement” could be re-written in quantitative terms (e.g. agrees to within some %)

It seems that Figures 7a and 7c-7f can all be estimated from Figure 6, so I recommend keeping only panel 7b which adds new information.

Plate 1: Could an arrow be added to point in the direction of the major mainland source region?

Figure 3: Why are NO concentrations below zero between 5-6 am on 11-Oct ?

Figure 4 and elsewhere, acronyms should be defined in the captions. The averaging time period should also be included (24 hrs?).

Figure 7 caption: give date

Figure 11 caption: explain how RIR is estimated

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