

## ***Interactive comment on “Examining the major contributors and controlling factors of ozone production in a rural area of the Yangtze River Delta region during harvest season” by X. Pan et al.***

### **Anonymous Referee #3**

Received and published: 6 January 2015

This paper presents measurements and modeling of ozone and its precursors from open burning of wheat residue in rural China and from pollution transported from the Shanghai megacity, including sensitivity analysis of ozone production to VOCs and NO<sub>x</sub> at different times and from various sources. In general the authors have performed a comprehensive analysis and presented the material clearly. The paper is interesting and suitable for ACP. However I would like the comments below to be addressed, in particular presenting more statistics within the text and strengthening a few of the arguments, especially related to furan and isoprene. Some clarifications and

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corrections are also needed.

Specific comments:

P30914, L4: Please state the dates of the field campaign in the abstract (month/year/duration).

P30914, L11: State the averaging period of the 100 ppbv (hourly?)

P30914, L20: Later in the paper we learn that 15 NMHCs were measured. Somewhere in the paper please compare your work to other studies of biomass burning to give a sense of what fraction of important ozone precursors were measured, and which were missing. Even in campaigns where 100+ NMHCs are measured from biomass burning, there are still dozens of unidentified compounds that can contribute to ozone formation. For this paper, which compounds were measured impacts how the '35 and 23%' are interpreted; the more NMHCs are measured probably the lower the solvent fraction becomes as the aromatic fraction becomes relatively less.

P30914, L11-13 and 21-22. L11-13 states that O<sub>3</sub> production was large when there was substantial NO<sub>x</sub>, but L21-22 states the opposite, that large NO<sub>x</sub> in the morning inhibited O<sub>3</sub> production. Please clarify.

P30915, L25: On the other hand, ozone production can be suppressed on short timescales due to titration with NO when NO<sub>x</sub> levels are high. Following from the above comment, perhaps present a brief discussion of impacts of high NO<sub>x</sub> on O<sub>3</sub>.

P30916, L15: State which year the measurements were made.

P30916, L24: Minor point but it's 'CO' on L24 but 'carbon monoxide' on P30917 L6. Define carbon monoxide as CO the first time it's mentioned then use CO thereafter. Make sure everything is defined (e.g., NO<sub>y</sub> on P30917, L13).

P30917, L18: Somewhere early on in the manuscript please state which specific NMHCs were measured (or refer the reader to Table 1). Which major O<sub>3</sub> major precursor

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sors are included and which were not measured? How might this affect your analysis?

P30917, L25: So presumably the 58-VOC mixture encompasses the 23 NMHCs/OVOCs presented here?

P30917, L26: Please state how many oxygenated VOCs were measured (or refer the reader to Table 1). Change 'MCAR' to 'MACR'. Define all acronyms.

P30917, L29: As well as the reference to Kudo et al., basic analytical information (precision, accuracy, etc.) still needs to be given here for the 15 NMHCs and 7 OVOCs.

P30918, L16: 'The missing data were linearly interpolated.' Please discuss what error/uncertainty this might introduce.

P30919, L5: Define RO<sub>2</sub> and phi separately rather than together.

P30920, L9: I believe this is the first time some specific NMHCs are being named (please name them sooner).

P30920, L13: What is the 'G-space'? What is 'F-peak'? Try to ensure that the text is accessible to readers who are less familiar with PMF.

P30920, L20: Define 'sigma units'.

P30920, L23: 'To better review the impact of emissions on the surface layer, only the footprint region of the air mass in units of residence time was demonstrated in the following analysis.' This sentence is a bit confusing because for me footprints and residence times do not intuitively go together, and the next sentence seems to define the footprint in terms of distance.

P30921, L7: The reader still doesn't know which year the measurements were made.

P30921, L9-11: Is the 147 ppb O<sub>3</sub> max also an hourly value? On L13 CO is presented as a daily average. On L16 it's not clear if the NO<sub>x</sub> and NO<sub>y</sub> means are hourly or daily. P30917 L20 says that the time resolution of the NMHC measurements is ~2 hrs ...

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is the average value of 200 ppbC on P30921 L19 a 2-hour average? Is the 451 ppbC maximum 'at 05:00' actually a 2-hour average? Because many different averages are presented in this paragraph, please state the time period (hourly, daily, etc.) each time an average is cited.

P30921, L11, 16, 19, etc.: Add an error bar to this average (and all others).

P30921, L12: What direction was the burning coming from?

P30921, L15-17: It may help to refer the reader to the wind roses in Figure 4 here; without wind direction plotted in Figure 2 it's difficult for the reader to connect the 'obvious enhancement' to southerly wind.

P30921, L15: High O<sub>3</sub> when air is transported from the megacity seems to contradict the previous sentence (highest O<sub>3</sub> during intensive open burning).

P30921, L25: This is the first time we're learning that the field campaign was in 2010. Please state the exact dates of the Expo so the reader can see the extent of the overlap.

P30921, L25: This sentence states that traffic increased, but the next sentence mentions emission controls and P30927 L11 suggests that NO<sub>x</sub> and NMHC emissions were actually reduced during the Expo. So did traffic actually decrease?

P30922, L10: What does 'daily increment' mean? Do you mean amplitude? Same comment on L13-14.

P30922, L14: Is '07:00' the average from '07:00-08:00'? Same question on L18-19. How the data are plotted can also be included in the Figure 3 caption. For NMHCs (Fig. 3g), if the time resolution is 2 hrs (P30917 L20) why are hourly data plotted?

P30922, L17: '38.6' seems to have too many significant figures given the very large error bar shown in Fig. 3c. Please add the error here and adjust the sig figs accordingly. Also this peak appears to be for 4 a.m., not the broader peak from 0:00-8:00 a.m.; please revise the text. Likewise on L22 state that 57 ppbv is the hourly peak of the

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broader range.

P30922, L16-19: Please state that you have shifted from discussing the red line in the first half of the sentence to the gray line in the second half of the sentence; currently it is confusing because the reader does not know that the two peaks are no longer about the red line.

P30922, L20: Why do these different peaks suggest transport rather than in situ production? Also what is the typical transport time from Shanghai to the site?

P30922, L21-25: In order for the general reader to follow these arguments you will need to define NO<sub>y</sub> and NO<sub>z</sub> earlier in the text (e.g. P30917 L13). Also add an error bar to 32.6 and reduce the number of significant figures as appropriate.

P30922, L24: Fig. 3e shows NO<sub>x</sub>/NO<sub>y</sub>, not NO<sub>z</sub>. Similar comment for P30923, L1.

P30923, L7: Add an error bar to the mean of 0.34 so the reader can see that it didn't vary.

P30923, L10: The morning error bars are large so 176.4 has too many significant figures. Please adjust and add its error bar. Also add an error bar to 48.6 and 62.8.

P30924, L6-7: Please add error bars to each mean that is reported. Same comment on L20, 25. Same comment on P30926 L5-6.

P30926, L7: The text makes it seem like the stagnant air mass persisted for 4 days (June 19-23) but Figure 2 indicates two separate pollution events on June 19 and 23. Should 'air mass was' be 'air masses were'?

P30926, L15: The runs are constrained by June 19 data but calculations are also presented for June 23 (L18). Were constraints from June 23 also used?

P30926, L25: This sentence is confusing because 'which' should be about NO<sub>x</sub> but is actually about NMHC/NO<sub>x</sub>. Please rework. Also 30-50 compared to 5 seems much larger than 'slightly' up.

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P30927, L2-3: In both lines change 'radial' to 'radical'.

P30927, L23: Is 1.4 similar to 2.0-2.2 (within the expected range) or is it actually statistically lower? An error bar on 1.4 would help (and on the values of 2.0 and 2.2 if they're available).

P30927, L27: '74.4' and '55.4' are too precise. Also on P30928 L1 a 20% difference is not 'slightly' higher.

P30927, L27+: These arguments don't seem to be adding up. The fraction of isoprene explained by OBB (74%) is surprisingly high to me, and it is also high compared to the YRDR inventory (54%; P30928 L2). Then on P30928 L3-4 the furan/isoprene ratio is too high, which is explained by isoprene being oxidized (so depleted). Please try to reconcile these arguments.

P30928, L6-7: How are you calculating the value of 3.5 from the Akagi paper? In their Table 1 column for crop residue they give an EF (g/kg) of 0.11 for furan and 0.38 for isoprene. So a furan/isoprene ratio would be  $0.11/0.38 = 0.29$  g/g. The mass ratio of 3.5 would be for isoprene/furan ( $0.38/0.11 = 3.5$ ). I haven't checked the Christian paper; is it also isoprene/furan? Is the 16.5 presented here isoprene/furan or furan/isoprene? Anyway it seems that the differences could be even larger than what was presented.

P30928, L7: 'photo-oxidation of isoprene in the summer season' seems speculative. Akagi et al. state the sources of the crop residue data; were these measurements also performed in summer? If so then this argument may not hold. Please investigate.

P30928, L7-9: 'and the furan/isoprene ratio would be approximately equal to that of previous studies if MVK/MACR were taken into consideration'. Taken into account how? If you believe this to be the case please provide evidence.

P30928, L15: You could further this argument by checking if the i-butane/n-butane ratio is consistent with LPG or NG.

P30928, L24: What was the benzene loading on Factor 1? Were you surprised to see

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benzene load onto a different factor than TEX?

Section 5.4.1: For each factor, each time a compound is associated with a specific source (acetonitrile for biomass burning, i-pentane for gas evaporation, NO<sub>2</sub> for fossil fuel combustion, etc.) please provide a reference.

P30929, L1-20: The verb tense changes from present to past in this paragraph. Also sometimes using words like 'could' and 'may' makes it unclear if the statement is a result or a speculation (e.g. L10-13; L19-20). Please rework.

P30929, L22: While you mean MVK+MACR (not MVK/MACR), earlier furan/isoprene was a fraction, so for clarity I suggest avoiding MVK/MACR if you don't mean a fraction and also to be consistent with L24-28. Same comment elsewhere in the paper and for other compound pairs.

P30930, L4: Are these mass-based ratios (like before with furan/isoprene)? If so please state this.

P30930, L5-6: 'oxygenated VOCs (including MVK and MACR) might also be preferentially present in the OBB plumes'. This statement seems speculative. What evidence is there for this?

P30930, L7: How were the numbers of 1.8 and 4.2 calculated? For example Akagi et al. don't provide MVK and MACR EFs for crop residue burning in their Table 1.

P30931, L9: There are too many significant figures on these numbers from the literature (they can't be known that accurately). Are these annual averages? If so for what year?

P30931, L13-14: Verb tense is changing again and the sentence is hard to follow. The paragraph is also a bit hard to follow . . . increased aerosols lead to decreased O<sub>3</sub>; O<sub>3</sub> is assumed to increase if aerosols are reduced; aerosol reduction leads to decreased AOD but increased actinic flux; high aerosol leads to decreased JO(1D); etc. Just it seems to go back and forth between impacts of increasing and decreasing aerosols;

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perhaps there is a smoother way to present this.

Table 1: Please also add max and min values and add units.

Figure 4: The units for the mixing ratios of O<sub>3</sub>, NO etc. need to be given.

Figure 6: The different lines also need to be defined in the legend (not just panel a).

Technical corrections:

P30914, L7: Suggest changing 'was observed' to 'was occurring'.

P30914, L14: Change 'potential' to 'a potential'.

P30915, L5: Change 'has' to 'have'.

P30915, L7: Omit 'evident'.

P30916, L1-4: The verb tense changes from present to past in this sentence.

P30916, L9: Change 'have' to 'has'.

P30916, L13: Change 'Quantitive' to 'Quantitative'.

P30916, L14: Change 'measurement' to 'measurement campaign'.

P30916, L22: Change 'area' to 'areas'.

P30917, L18: Change 'NMHCs' to 'NMHC'. Same comment on P30920, L7 and L11.

P30917, L18: Remove 'an' for this sentence to work.

P30918, L24: 'since NO<sub>2</sub> is known to exist at high concentrations comparable to O<sub>3</sub> at the observation site'. The wording in this sentence is a bit confusing.

P30920, L1: Do not capitalize 'Where'.

P30920, L6: Change 'numbers of NMHCs sources' to 'number of NMHC sources'?

P30920, L12: Change 'alkane' to 'alkanes'.

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P30920, L13: Change 'seed' to 'seeds'.  
P30920, L18: Capitalize all of 'HYSPLIT'.  
P30921, L1: Define FLEXPART.  
P30921, L10: Change 'dash' to 'dashed'.  
P30921, L10: Change 'the Fig.' to 'Fig.'  
P30921, L12: Change 'agriculture' to 'agricultural'.  
P30922, L22: Change 'boarder' to 'broader'.  
P30922, L23: Use a subscript in 'NO<sub>z</sub>'.  
P30923, L25: Change 'e.g.' to 'i.e.'  
P30924, L12: Could change 'Discussions' to 'Discussion'.  
P30925, L2: Change 'productions' to 'production'.  
P30925, L3: Omit 'the'.  
P30925, L15-16: To avoid repetition change 'observed at the observation site' to 'observed at the site'.  
P30926, L26: Change 'the observation in' to 'previous observations in the'.  
P30927, L9: Change 'from' to 'from the'.  
P30927, L20: 'Alkane' and 'alkene' should be plural.  
P30929, L4: Change 'as' to 'to be'.  
P30929, L15: Change 'air mass was' to 'air masses were'.  
P30930, L10: Change 'observation' to 'the observation'.  
P30930, L11-12: Change 'little amount' to 'small amounts'.

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P30930, L10-14: This is a run-on sentence. Please fix.  
P30930, L14-16: Please fix the grammar.  
P30930, L25: Omit 'refers to the paper,'.  
P30931, L19: Change 'will more' to 'will be more'.  
Figure 5: Caption needs a period.

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