

Interactive comment on “Measurements of higher alkanes using NO⁺ PTR-ToF-MS: significant contributions of higher alkanes to secondary organic aerosols in China” by Chaomin Wang et al.

Anonymous Referee #1

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General comments:

This paper describes the measurement of higher alkanes by NO⁺ PTR-ToF-MS at two sites in China and the authors showed the significant contribution of the higher alkanes to secondary organic aerosol (SOA) formation. I recognize that the measurement of the higher alkanes in ambient air is very challenging, so the data presented here would be precious. But I feel that there are two issues in the present paper.

Firstly, the authors seemed to fail to suppress the formation of O₂⁺ in the ion source (Figure S2). I think that the O₂⁺ reaction could substantially interfere with the ion signals of alkanes. In addition, I feel that the ratio of O₂⁺ to NO⁺ was not stable as

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far as I looked at Figure S2. The authors should pay attention to the intensity of O₂⁺ relative to the NO⁺ intensity.

Secondly, I feel that the diurnal variation of the OH exposure derived from isoprene chemistry method is strange (Figure S9). I cannot understand why the value is low during daytime compared with that in nighttime. The authors indicated two reference (Apel et al., 2002; Carlton et al., 2009), but I could not find the derivation of the OH exposure by "the isoprene chemistry method" in the references. The authors should show how the OH exposure by the isoprene chemistry method was calculated. I think that the low OH exposure during the daytime causes the low SOA formation from isoprenoids during the daytime, as shown in Figure 8(c).

Therefore, the paper is not acceptable until the two issues are resolved. Specific and technical comments are listed below.

Specific comments:

(1) Page 6, Line 113: In Figure S2, the authors showed that the relative intensity of O₂⁺ to that of NO⁺ was ~50 % (Fig. S2(a)) and ~15 % (Fig. S2(b)) under the conditions of U_s = 40 V and U_{so} = 120V. These conditions are not good because I think that the O₂⁺ reaction could substantially interfere with the ion signals of alkanes. I am concerned that the ratio of O₂⁺ to NO⁺ was not stable. The authors should mention the quality of the data of the alkanes presented in this paper.

(2) Page 6, Lines 130-131: I cannot agree to the argument by the authors that calibration factors were stable during the campaigns, because the normalized sensitivities of the n-C₁₅ alkane were scattered with a factor of 2. As far as I experienced, the normalized sensitivity is very stable. I feel that this instability of the normalized sensitivity may be related to the interference of the O₂⁺ reaction.

(3) Page 7, Lines 137-139: When I looked at the mass spectra in Figure S4, I found that the signal intensities of ¹³C-isotopologue of [M-1]⁺ are low. For example, the

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signal at m/z 282 should be 20 % of the intensity at m/z 281 for n-Eicosane. I wonder if the quantity was guaranteed or not in the present measurements using the NO+ PTR-ToF-MS instrument.

(4) Page 9, Lines 187-190: Some are good, but some are not good. The authors should mention the results correctly and explain the disagreement for some species. Were the concentrations from PTR-ToF-MS in Figs. S6 and S7 calibrated or calculated?

(5) Page 10, Lines 219-221: The degree of the chemical removal of hydrocarbons by the OH reaction was quite different at two sites, when we consider the concentration of OH (Figure S19). The authors should mention the results accurately.

(6) Page 10, Line 226: The data of naphthalenes were not shown anywhere in this paper.

(7) Page 11, Lines 239-242: I could not understand how the authors estimated the OH exposure clearly. Which value was used as the ratio of m+p-xylene to ethylbenzene at $t = 0$ (the emission ratio)? How was the OH exposure estimated by the oxidation process of isoprene? Why was the OH exposure estimated by the oxidation process of isoprene low during daytime compared with that in nighttime?

(8) Page 13, Lines 288-89: The diurnal variation of the estimated SOA produced from isoprenoids shown in Figure 8(c) is strange to me. In addition, I cannot understand the diurnal variations of the calculated SOA produced from higher alkanes, monoaromatics, naphthalenes, and isoprenoids in Figure 8(d). Why were those concentrations low during the daytime in spite of the fact that the production rates were calculated to be positive during the daytime (Figure S18(d)). Did the authors consider the dynamics (e.g., the movement of the boundary layer) into the calculation? If so, explain in the text.

(9) Page 32, Figure 8(d): The diurnal variation of the measured SOA in Figure 8(d) seems to be different from that in Figure S11(b). Is it OK?

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(10) Page S5, Line 106: Explain “isoprene chemistry method”.

(11) Page S7, Line 129: Which equation was used in the present paper, eqn. (1) in Page 11, Line 235 or eqn. (7) in Page S7, Line 129? Don't make readers confused.

Technical comments:

(1) Page 4, Line 72: Anh et al., 2008. (“et al.” is missing)

(2) Page 4, Line 83-84: Erickson et al. (2014) did not use NO⁺ as the reagent ion. Don't make readers misread. Same comment to Page 5, Line 108.

(3) Page 6, Line 125: Corbin et al., 2015. (Delete “C.”)

(4) Page 9, Line 208: Table 1 → Table 2

(5) Page 14, Line 319-Page 15, Line 347: I feel it strange that some papers are cited in “Conclusions”. If the authors want to cite the papers, I think that the authors change “Conclusions” to “Concluding remarks”.

(6) Page 17, Line 404: “C. Corbin, J.” → “Corbin, J. C.”

(7) Page S6, Line 107: Figure S8 → Figure S9

(8) Page S7, Lines 134-143: These are mentioned in the text (Page 11, Line 249-Page 12, Line 259)

(9) Page S17, Figure S9: “expousre” → “exposure”

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