

General comments:

This manuscript investigated the emissions of various primary pollutants and photochemical evolution from burning three types of agricultural residues (corn, rice and wheat straws) by using a 30m³-smog chamber. The experimental design is reasonable, the results are reliable, and the conclusions are convincing. Considering the rare information on primary emissions and photochemical evolution of agricultural residues burning, the original data presented in this manuscript are very important for comprehensively understanding the impact of the burning on the air quality, especially in China. The manuscript is well organized, and hence this reviewer recommends the manuscript be published in the journal.

Reply: Thanks for the positive comments. We have revised our manuscript after carefully reading the following constructive suggestions.

Specific comments:

[1] Both biomass burning and domestic coal combustion have been recognized to make evident contribution to deteriorating regional air quality especially in North China. If the authors had compared with the emission strengths between the biomass combustion and domestic coal combustion, the result would be more attractive. The authors only compared with the SO₂ emission factors between the biomass burning and coal cake combustion, however the emission factor of coal cake might be outdated, because raw bituminous is currently prevailing for cooking and heating in rural areas. The emission factors of various pollutants from combustion of raw bituminous in domestic stove have been reported (e.g. SO₂ emission factors of 4.16-1.36 g SO₂ kg⁻¹, Du, Q. et al. (2016), An important missing source of atmospheric carbonyl sulfide: Domestic coal combustion, *Geophys. Res. Lett.*, 43(16), 8720–8727, doi:10.1002/2016GL070075; NMHCs (57 species) average emission factor of 2981.1 mg kg⁻¹, Liu et al.(2017), Emission of volatile organic compounds from domestic coal stove with the actual alternation of flaming and smoldering combustion processes, *Environmental Pollution*

221, 385-391). Although the emission factors of SO₂ from the burning of corn and wheat straw is about 3-6 times less than that of coal combustion and of NMHCs is comparable to each other, the emissions of these pollutants from the biomass burning might largely exceed those from domestic coal combustion because the amount of the biomass burning might be one magnitude greater than that of domestic coal consumption in China. Therefore, greater attention should be paid on the emission of biomass burning for improving the air quality in China.

Reply: Thanks. We agree that the comparison of primary emissions between agricultural residues burning and domestic coal combustion would help policy makers for the control of air pollution. As suggested, we have updated emission factors for coal combustion in the latest literatures, and added the following words in the revised “Conclusions” part:

“Both agricultural residues burning and domestic coal combustion have been recognized to contribute substantially to the deteriorating regional air quality especially in rural areas of China (Pan et al., 2015; Liu et al., 2016; Zhu et al., 2016). The emission factors of the speciated NMHCs, PM and SO₂ from combustion of raw bituminous, which is currently prevailing for cooking and heating in rural areas, have been reported to be 0.56-5.40, 25.49±2.30 and 2.43-5.36 g kg⁻¹, respectively (Du et al., 2016; Li et al., 2016; Liu et al., 2017). Annually burned crop residues and domestic coals were estimated to be 160 Tg (Li et al., 2016) and 99.6 Tg (NBSPRC, 2014) in China. Therefore, with the emission factors of the speciated NMHCs (2.47-5.04 g kg⁻¹), PM (3.73-6.36 g kg⁻¹) and SO₂ (0.07-0.99 g kg⁻¹) measured for agricultural residues burning in this study, agricultural residues burning might emit more NMHCs, but less primary PM and SO₂ than domestic coal burning on a national scale.”

[2] The concentration of OH radical indirectly obtained by tracing the first order decay rate of toluene should represent its average concentration during the whole irradiation, why did you use the OH exposure of (1.87-4.97)×10¹⁰ molecule cm⁻³ s? Are your sure

the lifetime of OH radical in the chamber is only 1s? I suggested to use the unit of average concentration $(1.87-4.97) \times 10^{10}$ molecule cm^{-3} .

Reply: In fact, the average OH concentration in this manuscript was calculated every 2 minutes by continuous monitoring of toluene concentration through PTR-TOF-MS, thus the average “OH exposure” every 2 min was calculated as the product of average OH concentration and the time interval. OH exposure, indicating the atmospheric oxidation power that a pollutant undergoes, is a parameter that has been widely used in the chamber studies (e.g., Hennigan et al., 2010; Tiitta et al., 2016; Tkacik et al., 2017). In the revised manuscript, we have revised the manuscript to include this detailed information about how the average OH concentration was calculated: “The decay of toluene measured by PTR-TOF-MS was used to derive the average OH radical concentrations for every 2 min during each experiment, and the integrated OH exposure was calculated as the product of the OH concentration and the time interval.”

[3] Although the contribution of the 20 NMOGs to the SOA only accounted for 5-27.3% of the observed SOA mass, the increase of the SOA mass might not solely be ascribed to the aqueous-phase oxidation of alkenes, because the oxidation of the POM with more oxygen can also make evident contribution.

Reply: Thanks for the comments. The possible contribution from the oxidation of POM has been included in the revised manuscript, and some other reasons for the discrepancy have also been added:

“It is noted that although over 80 VOCs species were quantified by the GC-MSD/FID and the PTR-TOF-MS in this study, only 20 species among them were taken into the SOA prediction because of the lack of published data for SOA yields. The unaccounted VOC species might be a reason for the discrepancy. On the other hand, as indicated by Deng et al. (2017), SOA yields obtained from chamber studies in purified air matrix might be lower than that in real ambient air matrix. Consequently, using SOA yields from studies in purified air matrix might also under predict SOA yields in the complex

biomass burning plume matrix. Moreover, oxidation of particulate organic matters (POM), like semi-volatile organic compounds (SVOC) and intermediate volatility organic compounds (IVOC), would also contribute substantially to SOA formation (Presto et al., 2009; Zhao et al., 2014), yet this is not accounted for in our prediction..”

[4] (Page 16, line 366-368) The two OA enhancement ratios reported were evidently less than those determined in this study, why did you concluded that the OA enhancement ratios determined were higher than those (0.7-2.9) for the combustion of vegetation, and comparable to those (0.7-6.9) for wood burning?

Reply: The OA enhancement ratio in our study should be 2.4-7.6 rather than 2.4-76 in this sentence. We are quite sorry for this typo and have corrected it in the revised manuscript.

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