

#2 Review comments: "Multi-pollutants emissions from the burning of major agricultural residues in China and the related health-economic effect assessment" by Li C. et al..

This study investigates the emission factors of multi-pollutants from five major crop residues in China, and tries to estimate emission inventory and their corresponding health-economic effect. This paper is well organized and presents some interesting data. However, detailed explanations about the design should be given to ensure the data quality.

Answer: Thanks for your carefully review!

Question 1: When the crop residues were dehydrated at 100 degree C for 24 hrs, what are the impacts to the emission factors and PM compositions?

Answer 1: Pretreatment of biomass fuel in burning simulation is a practical and necessary procedure to ensure the result can be comparable with other studies under the defined conditions, like dehydration at 100 °C for 24 hrs to ensure water content of the residue within 2 wt. %, which has been applied in many burning studies (Hayashi et al., 2014; Huo et al., 2016; Li et al., 2015; Oanh et al., 2011; Zhang et al., 2008; Zhang et al., 2011). Water content of residue is a variate response to the smoke particle emissions and burning efficiency of biofuel (Hayashi et al., 2014; Oanh et al., 2011), and residue moistness has been shown to be positively correlated with particle emissions in range of 5~35 wt.%. However, empirical emission inventory calculation has to simplify the water content of residues to get the final dry matter, thus we designed our combustion method by dehydration the biomass fuel in front, besides, the residues we collected from field have water content of less than 5 wt.% on average (wheat: 3.7 wt.%, rice: 4.4 wt.%, corn: 6.3 wt.%, soybean: 5.1 wt.%, cotton: 4.6 wt.%), the dehydration to get water content within 2 wt.% will have much weaker influence on the chemical emissions.

Question 2: There are huge variations on EFs of crop residues, and they depend on lots of factors such as, sources of crop residues, burning temperature, burning efficiency etc. What are the differences between chamber study and open burning? As the burning last about 1 min only (in chamber study), can it represent the real open burning results? Moreover, what is the dilution ratio in the chamber study?

Answer 2: Chamber simulation has defined advantages over the field burning study, but it is also the paradox that chamber work can hardly reproduce the practical burning that be impacted by many influences in the field. To the emission factor measurements, we have to trade-off and simplify some impacts reasonably, for example burning efficiency, water content, and meteorological parameter etc, however, we don't mean these impacts can be neglected. Previous work told result from lab simulation will be reasonably agree with that from field burning under fixed combustion efficiency, while some particulate compounds like EC and PAHs may be overestimated in chamber study due to high and concentrated mass loading of PM and their impact on the measurements (Dhammapala et al., 2007). We controlled the preparation time to be less than 5 min (<2 min for the burning, ~3 min for chamber stabilization), minimizing the aging and diffusion/deposition of the primary emissions, and under the fixed combustion efficiency, seldom studies ever considered burning time as an impact factor on emission factor estimation (Dhammapala et al., 2007; Zhang et al., 2008). The chamber has a volume of 4.5m³ mass concentration for smoke PM_{2.5} at initial time

in the chamber are 10~30 mg m⁻³, during sampling and monitoring from the chamber, the dilution ratio for is 10:1~50:1 (details in supporting information).

Question 3: The detection limits (MDL) for all analysis should be provided.

Answer 3: The detection limits (DL) were added in the manuscript as below presented, water soluble species were measured using IC techniques, and DLs were about 0.5~3.5 ng mL⁻¹.

Table 3 Detection limit and recovery rate of water soluble species measured by IC

| Water soluble species | ng mL ⁻¹ | recovery rate |
|---------------------------------------|---------------------|---------------|
| Na ⁺ | 0.59 | 99.1% |
| NH ₄ ⁺ | 0.63 | 96.5% |
| K ⁺ | 1.65 | 98.8% |
| Ca ²⁺ | 3.33 | 103.0% |
| Mg ²⁺ | 2.07 | 101.5% |
| F ⁻ | 0.72 | 99.3% |
| Cl ⁻ | 0.47 | 99.6% |
| NO ₂ ⁻ | 1.11 | 92.5% |
| NO ₃ ⁻ | 0.93 | 101.0% |
| SO ₄ ²⁻ | 0.68 | 99.0% |
| MeOH ⁺ | 1.12 | 94.4% |
| MMAH ⁺ | 0.59 | 97.3% |
| MEAH ⁺ | 1.03 | 106.1% |
| TEOH ⁺ | 1.13 | 95.0% |
| DEAH ⁺ + TMAH ⁺ | 0.61 | 103.6% |
| DMAH ⁺ | 1.37 | 104.2% |

OC-EC was measured using Thermal/Optical Carbon Analyzer, as aerosol samples were deposited onto the quartz filter, detection limits for total OC and EC were 0.82 and 0.22 µg C cm⁻². Elements (As, Zn, Pb, Cd, Cr, Ni, V, and Al) were measured by ICP-OES, DLs were within 0.2~2.1 ng mL⁻¹. PAHs and Phenols were measured using GC-MS, we prepared standard solutions with 6 concentration gradients of 0.020, 0.04, 0.10, 0.15, 0.25, 0.40 ppm for 16 target mixed PAHs, and 0.05, 0.10, 0.25, 0.50, 1.50, 4.00 ppm for 5 target mixed Phenols, all reagents used were of highest grades, and water used were Mili-Q one. Before all the measurements, recovery tests for the chemical components were conducted.

Table 4 Detection limit and recovery rate of multi-pollutants

| Elements | Molecular weight | recovery rate | DLs (ng mL ⁻¹) |
|-------------|------------------|---------------|----------------------------|
| As | 74.9 | 93.0% | 2.0 |
| Zn | 65.4 | 98.3% | 0.2 |
| Pb | 207.2 | 99.7% | 1.5 |
| Cd | 112.4 | 96.7% | 0.1 |
| Ni | 58.7 | 102.0% | 0.2 |
| Cr | 52.0 | 94.9% | 0.2 |
| V | 50.9 | 98.7% | 0.5 |
| Al | 27.0 | 95.7% | 0.9 |
| PAHs | Molecular weight | recovery rate | DLs (ng mL ⁻¹) |
| naphthalene | 128 | 97.0% | 0.8 |

| acenaphthylene | 152 | 98.5% | 1.8 |
|-------------------------|------------------|---------------|----------------------------|
| acenaphthene | 154 | 96.2% | 1.1 |
| flourene | 166 | 88.3% | 1.0 |
| anthracene | 178 | 96.9% | 0.5 |
| phenathrene | 178 | 97.9% | 0.9 |
| flouranthene | 202 | 94.4% | 1.0 |
| pyrene | 202 | 96.1% | 0.5 |
| benz[a]anthracene | 228 | 96.7% | 0.1 |
| chrysene | 228 | 94.1% | 2.0 |
| benzo[a]pyrene | 252 | 95.3% | 1.0 |
| benzo[b]flouranthene | 252 | 88.7% | 0.9 |
| benzo[k]flouranthene | 252 | 84.9% | 0.9 |
| benzo[g,h,i]pyrene | 276 | 84.9% | 0.6 |
| indeno[1,2,3-cd]pyrene | 278 | 90.9% | 0.6 |
| dibenz[a,h]anthracene | 276 | 84.9% | 0.8 |
| Phenols | Molecular weight | recovery rate | DLs (ng mL ⁻¹) |
| phenol | 94 | 93.0% | 0.5 |
| 2-methoxyphenol | 124 | 82.0% | 2.0 |
| 4-ethylphenol | 122 | 84.5% | 4.0 |
| 4-ethyl-2-methoxyphenol | 152 | 86.1% | ~5.0 |
| 2,6-dimethoxyphenol | 154 | 87.5% | ~5.0 |

Line 290: add in the manuscript “Sampled filters were ultrasonically extracted with 15.0 mL deionized water (Mili-Q water, 18.2 MΩ cm), extracted solutions were filtrated using 0.2 μm filters before injected into IC for measurement. Detection limits (DLs) for the ions and aminiums were within 0.5~3.5 ng mL⁻¹, the correlation coefficients for all calibration curves were better than 0.99, and recovery rates for aminiums were in the range of 93%~106% (see in SI, Table S1). Details for the aminium measurements can be found in the work of Tao et al. (2016).

Line 303: add in the manuscript “The following wavelength lines of the ICP-OES analysis were used: As 189.042, Pb 220.353, Cd 228.802, Cr 205552, Ni 231.604, V 311.071, Zn 206.191, and Al 394.401. All reagents used were of highest grades, and recovery tests were conducted with standard additions, recoveries of each element were in the range of 93%~102% (see in SI, Table S1).”

Line 317: add in the manuscript “using an Agilent 6890 Series gas chromatography system coupled with a HP 5973 Mass Selective Detector (GC-MS, Agilent Technologies, Wilmington DE) . A DB-5ms (30 m × 0.32 mm × 0.25 mm, Agilent 123-5532) column was installed. The temperature programs were presented as follows: initially at 40 °C, hold for 4 min, to 150 °C at 20 °C min⁻¹, then to 280 °C at 5 °C min⁻¹, hold for 10 min. The interface temperature was kept at 280 °C, the MS was operated in electron impact mode with an ion source temperature of 230 °C, and the high-purity helium (99.999%) carrier gas was maintained at a constant pressure of 16.2 psi with a flow of 2.0 mL min⁻¹. The calibration curves were optimized to be better than 99.9%. Prior to the measurements, PAHs and Phenols recovery studies were undertaken, and recoveries

were acceptable with rates of 82%~99% (see in SI, Table S1). In addition, Phenanthrene-d10 (Phe-d10) as internal standard surrogate was added into the PAHs mixture, recovery rate of which was 94%.”

Line 342: add in the manuscript “The instrument detection limits for total OC and EC that deposit on the filter are 0.25 and 0.12 $\mu\text{g C cm}^{-2}$. Moreover, environmental EC in aerosol is a mixture of compounds from slightly charred, biodegradable materials to highly condensed and refractory soot, different EC materials have distinct different thermodynamic properties, study found char-EC decomposes much rapidly than soot when exposed to chemical and thermal oxidation, e.g., EC decomposition temperatures in air increased from $\sim 520^\circ\text{C}$ for char to $\sim 620^\circ\text{C}$ for soot, and exceeded 850°C for graphite, thus, regarding to different oxidation temperatures,”

Question 4: It is interesting to determine char and soot, however, the temperature protocol is IMPROVE, but not NIOSH. Any calibrations have been performed with pure soot and char (standard)?

Answer 4: Yes, as you mentioned, most of the studies discriminated Char-/soot-EC from carbon analyzer based on TOR (Thermal-optical reflectance) with IMPROVE protocol, it is empirical function to define char-EC as EC1-PC and soot-EC as EC2+EC3, we did not calibrated the performance of the carbon analyzer used in soot/char classification, but we ever characterized diesel soot particles (diesel engine exhaust) and wood-char (600°C power plant) using the OC-EC analyzer (TOT-NIOSH) combined with TG-MS (Thermalgravimetric-MS analysis) and chemical analysis, the result was given below:

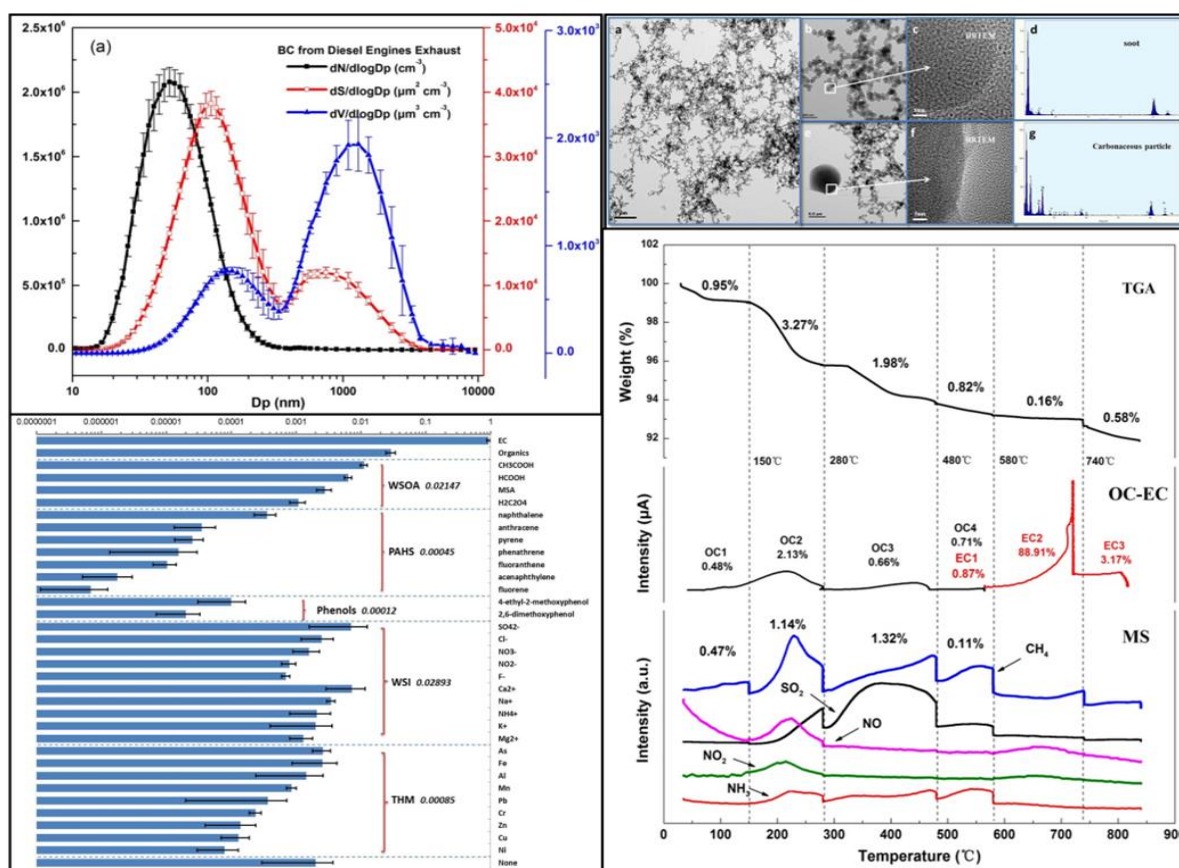


Figure 1 characterization of soot particles (size distribution, morphology, and chemical profiles)

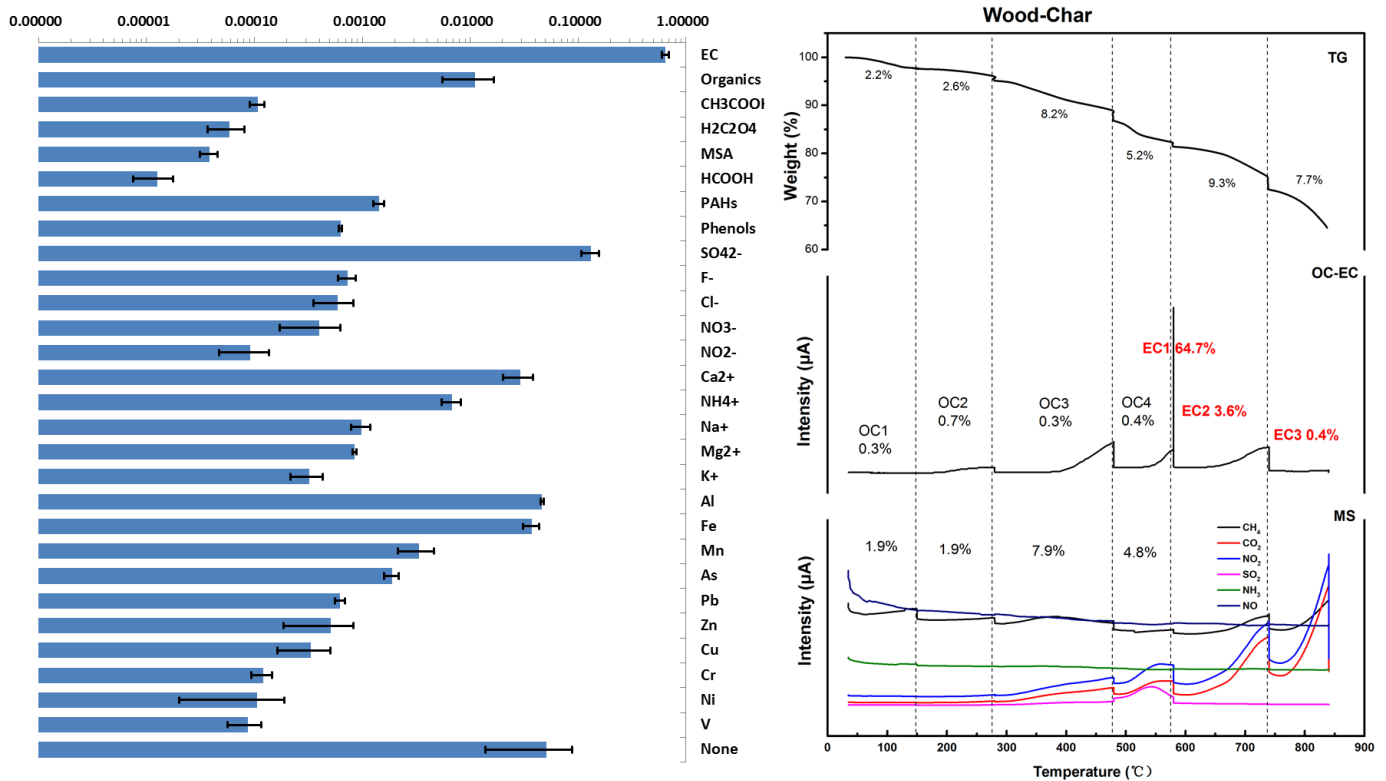


Figure 2 Chemical profiles and TG-MS-Carbon analysis of wood-char

It was obviously soot deposited into EC2 and EC3 fractions ((EC2+EC3)/EC~1.0), while char responded to EC1 ((EC1-PC)/EC~0.94), it seems that NIOSH protocol method is also possible to measure char-/soot-EC of aerosol. Han et al (2016) compared the OC-EC measurements between TOT and TOR methods with different protocols (IMPROVE, IMPROVE-A, EUSAAR-2 or modified NIOSH), good correlations among carbon results measured with the various methods were observed, but TOT-NIOSH method may overestimate PC fraction sacrificing EC part compared with TOR-IMPROVE method, thus different methods have impact on OC-EC split. However, char-/soot-EC were classified by different oxidation temperature, carbon analyzer based on TOT-NIOSH method in this study was set to operate at the same temperature gradient as Han et al (2007; 2009; 2016) ever performed, that means neglecting the impact of the methods on OC-EC split, calculation of char-EC and soot-EC can be also feasible in this study, but this method may underestimate char-EC, leading to lower char-EC/soot-EC ratio. More precise experiments will be conducted in the future to investigate the applicability of TOT-NIOSH method in char-/soot-EC measurements.

Question 5: Please describe how to screen agricultural fire from MODIS daily fire products? What are the selecting criteria?

Answer 5: Data of mainland agricultural fire sites was derived from the daily report of the Ministry of Environmental Protection of China (MEPC) (website: <http://hjj.mep.gov.cn/jgjs/>). MEPC selected MODIS (Moderate Resolution Imaging Spectroradiometer) Thermal Anomalies/Fire products based on space observations of NASA's Terra and Aqua satellites. Fire detection algorithm was used MODIS Thermal Anomalies/Fire daily products (MOD 14/MYD14) through brightness temperature derived from the MODIS 3.95 and 11.0 μm channels, of which 3.95 μm channel to detect fire sites via infrared radiation, and 11.0 μm

channel to derive cloud and land background temperature. The product is tile-based, with each product file spanning one of 460 MODIS tiles, of which 326 contain land pixels, and in 1 Km gridded cell over each daily (24 h) compositing period. Two observations per day are possible with the Terra overpass at 10:30 local time and the Aqua overpass at 13:30 local time. Version 4 of MODIS fire detection data was used combining with 1 Km land cover dataset (Global land cover-China), active fire detection that occurred on the land cover classes defined as “farm” and “mosaic of cropping” was identified as crop residue burning in fields.

Question 6: In this study, five crop residues were selected to determine their multi-pollutants emission factors, but there are other major crop residues not considered in this study, e.g. sugarcane, barley etc. There should be a reason to explain why such crop residues were not considered and how to determine the emission inventories in some provinces (with high sugarcane and barley production).

Answer 6: Thanks for your comment, the article presents pollutant emissions from major agricultural residues burning in China, and wheat, rice, corn, soybean, and cotton are surely the dominated agricultural productions in China, which contribute over 90 wt.% of national residue yields from China Statistical Yearbook (NBSC, 2013; Qin and Xie, 2011). Field burning of wheat, rice, and corn straws burning was the most common agricultural open burning and drawn much attention. Some crops like sugarcane and barley are regional cash crops that are mainly planted in Guangdong, Guangxi, and Hainan, where the total residue productions make less than 8 wt.% of national ones, even in the specific province themselves, sugarcane and barley residues contribute less than 30 wt.% of the straws on average (NBSC, 2013). Besides, this study focused on giving the updated and comprehensive emission factors of the most field burnt agricultural straws via chamber simulation method, we are quite sorry that we cannot take all the residues into consideration.

Question 7: There is some typo errors found in the manuscript: Line 215, “costume-built” should be “custom-built” Line 330, “Corp straw” should be “Crop straw”

Answer 7: Thanks for your comment, we have fully checked and modified the manuscript.

Line 224: “custom-built” has been corrected

Line 390: “Crop straw” has been corrected

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