Reviewer 3

This manuscript is a nice piece of work describing the emission of nitrogen containing aromatic compounds (NAC) from the use of cookstoves. The authors aim to understand the contribution of these species to the light absorption of organic matter in PM2.5 at the wavelength of 365 nm. The authors found that much higher contribution of NAC light absorption to PM2.5 in quartz fiber backup filters than in PTFE front filters, suggesting that NAC may be an important group of light absorbing compounds in the gas phase. In addition, the authors found the NAC compounds targeted in this manuscript (Mw < 300) are less important for the light absorption of PM2.5 bound organic matter at least from cookstove emissions, and indicate that larger molecules with Mw > 500 are responsible for the light absorption of organic matters. The manuscript is well written, and I recommend publication of this manuscript after addressing minor technical corrections outlined below.

Reply:

Thanks for the reviewer's comments, and we'll reply these point by point in the reviewer's specific comments.

Specific comments:

1. If it is possible, the authors should present all NAC in emission factors (g kg^{-1}) rather than in mass concentrations (μg m^{-3}). Emission factors are more useful than mass concentrations as they can be used for emission control strategies directly.

Reply:

In this work, the target is to characterize the composition, structures, and light absorption of NACs from cookstove emissions. The results will improve our understanding on BrC chromophores and sources. To exhibit NACs composition and absorption, their mass concentrations in filter samples should be provided.

As we mentioned in the manuscript, the emissions of OC and EC for the same cookstove tests were reported in our previous work (Xie et al., 2018) (lines 150-151). The emission factors (EFs) of total NACs (g kg^{-1} dry fuel) can be obtained from the EFs of OC and the mass ratios of total NACs to OC. In the revised manuscript, the EFs of total NACs were given in Table S5.

Table S5. Average emission factors of total NACs and OC

Fuel &Test phase	**Red Oak**		**Charcoal**	
	CS	**HS**[a]	**CS**	**HS**
		Front filter (Q_f)		
Sample number	18	17[b]	15	15
total NAC (mg kg^{-1} dry fuel)	1.18 ± 0.58	1.23 ± 0.69	0.79 ± 0.65	1.40 ± 0.65
OC (mg kg^{-1} dry fuel)	244 ± 170	340 ± 326	179 ± 114	619 ± 368
		Backup filter (Q_b)		
Sample number	18	17[b]	14[b]	15
total NAC (mg kg^{-1} dry fuel)	0.55 ± 0.24	0.61 ± 0.38	0.62 ± 0.53	1.83 ± 0.79
OC (mg kg^{-1} dry fuel)	30.5 ± 17.6	38.2 ± 24.8	66.5 ± 38.9	196 ± 96.2

[a] Including three SIM phase samples from the 3-stone fire; [b] one filter sample was missed for analysis.

“*The EFs of total NACs shown in Table S5 were obtained by multiplying the EFs of OC and tNAC$_{OC}$%.*” (Lines 218-219)

2. Line 171: ng _L should be ng/μL or ng μL-1.

Reply:

Revised as suggested. (Line 188)

3. Line 214 onwards: This assumes that the backup quartz fiber filter can trap all the gas phase compounds and does not have a breakthrough at all. A better way to estimate the artifact of a filter sampling system is to utilize a denuder in front of a PTFE filter for gas sampling and place a quartz fiber filter after the PTFE to correct a negative artifact from blown-off. It would be good if the authors discuss briefly here about the potential usage of the denuder for the artifact correction in addition to the backup quartz fiber filter.

Reply:

Thanks for the reviewer’s suggestions.

The backup quartz filter was typically used to evaluate the adsorption of gaseous organics (“positive artifact”) on filter media. This method does not assume that the backup filter can trap all the gas-phase compounds. We mentioned that the gas-phase NACs were not measured in this study (lines 344-347), and concluded “*Further studies are warranted to investigate the gas/particle distribution of NACs in the ambient and source emissions.*” (Lines 481-482)

In the revised manuscript, we added a few descriptions on the use of a denuder to avoid positive artifacts and its potential issues.

“*A denuder upstream of the filter for gas sampling was used to avoid positive artifact in several studies (Ding et al., 2002; Ahrens et al., 2012). This approach can generate large negative artifacts by altering the gas-particle equilibrium after the denuder, and a denuder efficiency of 100% might not be guaranteed (Kirchstetter et al., 2001; Subramanian et al., 2004).*” (Lines 238-242)

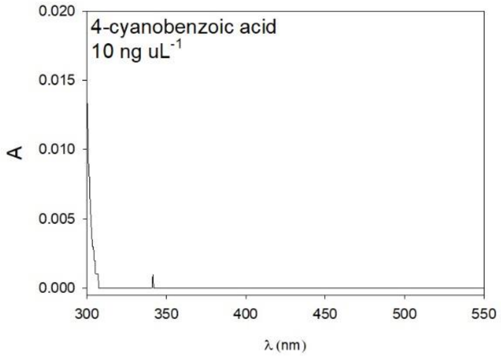
4. Line 283: In Table S3, the authors suggest C8H5NO2 as 3-cyanobenzoic acid. This is commercially available from several chemical suppliers, and it can be positively identified if C8H5NO2 correspond to the authors’ suggestion. I ask the authors to purchase the standard compound and quantify it instead of using a surrogate compound.

Reply:

Thanks for the reviewer’s suggestion.

After testing the three isomers of cyanobenzoic acid (2-, 3-, and 4-cyanobenzoic acid), the $C_8H_5NO_2$ molecule from cookstove emissions was identified as 4-cyanobenzoic acid. So, the mass concentration and absorption of $C_8H_5NO_2$ were quantified using 4-cyanobenzoic acid.

We have updated the tables and figures with $C_8H_5NO_2$ throughout the manuscript. As shown in the figure below, 4-cyanobenzoic acid has no light absorption at > 350 nm. Thus, the contribution of $C_8H_5NO_2$ to Abs$_{365}$ of sample extracts is 0.



5. Fig S5: The mass spectrometric conditions and ionization methods used to obtain MS2 spectra for some compounds shown in Fig S5 are very different from ones shown in Fig S4, and they are not comparable at all. I ask the authors to remove those (EI and ESI+) from Fig S5 as they cannot be compared to each other.

Reply:

The MS-MS spectra of $C_8H_7NO_4$ and $C_9H_9NO_4$ showed the loss of OCN (Fig. S4g, m), suggesting a structure of benzoxazole/benzisoxazole or the presence of cyanate (−O−C≡N) or isocyanate (−O=C=N) groups. To identify the structure of the OCN group, the MS and MS-MS spectra of four standard compounds, including phenyl cyanate (C_6H_5OCN), benzoxazole (C_7H_5NO), 4-methoxyphenyl isocyanate ($CH_3OC_6H_4NCO$), and 2,4-dimethoxyphenyl isocyanate [$(CH_3O)_2C_6H_3NCO$] were obtained from Xie et al. (2019) and shown in Fig. S5 (i-n). These compounds do not have a phenol structure and cannot be detected using ESI under negative ion mode. Fig. S5 (i-n) suggest that the loss of an OCN group only happens during the fragmentation of phenyl cyanate. If Fig. S5 (i-n) is removed, we cannot identify the phenyl cyanate feature for $C_8H_7NO_4$ and $C_9H_9NO_4$ (Lines 380-386).

"*The MS-MS spectra of $C_8H_7NO_4$ eluting at 8.14 min (Fig. S3e) and $C_9H_9NO_4$ eluting at 9.22 min (Fig. S3j) indicate the loss of OCN (Fig. S4g, m), suggesting benzoxazole/benzisoxazole structure or the presence of cyanate (−O−C≡N) or isocyanate (−O=C=N) groups. Mass spectra of selected standard compounds (Fig. S5i-n) in our previous work (Xie et al. 2019) show the loss of an OCN group only happens during the fragmentation of phenyl cyanate. Thus, the $C_8H_7NO_4$ and $C_9H_9NO_4$ isomers containing OCN indicate a phenyl cyanate feature.*"

Xie et al. (2019) identified the phenyl cyanate structure for NACs from open biomass burning in a same way. Therefore, we kept these mass spectra in supplementary information.

References

Xie, M., Shen, G., Holder, A. L., Hays, M. D., and Jetter, J. J.: Light absorption of organic carbon emitted from burning wood, charcoal, and kerosene in household cookstoves, Environmental Pollution, 240, 60-67, https://doi.org/10.1016/j.envpol.2018.04.085, 2018.

Xie, M., Chen, X., Hays, M. D., and Holder, A. L.: Composition and light absorption of N-containing aromatic compounds in organic aerosols from laboratory biomass burning, Atmospheric Chemistry and Physics, 19, 2899-2915, 10.5194/acp-19-2899-2019, 2019.