Reviewer 1

Xie et al. identified and quantified individual nitrogen-containing aromatic compounds (NACs) found in cookstove aerosol produced from water boiling tests. The study focused on two different fuels, charcoal and red oak, and mainly compared and contrasted emissions of NACs from cold start and hot start phases of the WBT. A unique aspect of this study is a focus on filter artifacts by comparing NACs on a quartz fiber filter placed downline of a PTFE membrane. In addition, they quantified the absorption of individual NACs at 365 nm based on their measured concentrations. The authors identified 17 different structures of NACs from their MS-MS spectra. The main conclusions of this study are that the backup quartz fiber filter concentrations of NACs were very high, sometimes even larger than on the front PTFE filter highlighting the importance of understanding these sampling artifacts for quantification of semivolatile species better. They also conclude that the NACs in this study make up less than 5% of the extractable absorption at 365 nm on the PTFE filter.

General comments: The results of this paper should be published because this study quantifies particulate emissions of NACs from cookstoves, which is understudied. The results also demonstrate the need to understand sampling artifacts from filters when they are used for quantitative analysis. However, some of the key conclusions of the paper may be misleading for the reader. For example, it is concluded that <5% of the extractable absorption is from NACs and they not significant brown carbon chromophores in cookstove smoke. However, much higher percentages were observed on the back up quartz filter, some of which may be in the particle phase in the atmosphere.

Reply:

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

Here we just want to clarify that NACs were analyzed only for quartz filter samples (front and backup filters, Q_f and Q_b). PTFE filters were commonly used for gravimetric analysis, but were rarely extracted using organic solvents. The installation of a backup quartz filter (Q_b) behind a PTFE filter in parallel to a bare quartz filter (Q_f) was typically used to estimate the adsorption of gaseous OC ("positive artifact") on the main (or "bare") quartz filter (Subramanian et al., 2004; Watson et al., 2009). This Q-QBT approach presumes that the upstream PTFE filter adsorb no organic gases, and then Q_b is exposed to organic vapor with the same concentration as Q_f. It has been shown to provide a robust estimate of the positive artifact on Q_f OC (McDow and Huntzicker, 1990; Turpin et al., 1994).

In section 2.2 (lines 166-167), we have mentioned that the Q_f and Q_b sample extraction and subsequent analysis for NACs were conducted as described in Xie et al. (2019).

To avoid the confusion, the original expressions

"*to evaluate the potential for sampling artifacts of NACs in* $PM_{2.5}$." (lines 120-121)

"*Adsorption artifact was evaluated using a quartz-fiber back-up filter* (Q_b) *installed downstream of the PTFE filter during* $PM_{2.5}$ *sampling.*" (lines 143-144)

have been changed into

"*to evaluate the potential for sampling artifacts of $PM_{2.5}$ NACs on the bare quartz filter in parallel.*" (lines 119-120)

"*The adsorption artifact of Q_f was evaluated using a quartz-fiber back-up filter (Q_b) installed downstream of the PTFE filter during $PM_{2.5}$ sampling.*" (lines 147-148)

Specific comments:

1. There are some well-documented problems with WBTs, mostly arguing that their combustion efficiencies don't match those in the real world (Johnson et al., 2008, 2010). If the combustion efficiency in real homes is lower, this could result in less NACs due to less flaming and lower NOx. Given this, it would be helpful to have a measure of combustion efficiency, such as modified combustion efficiency, so that it can be compared with field measurements in the future. This may be possible, given the paper mentions gaseous pollutants were measured (Line 140). Even without this, it would be helpful to have more of a description of the cookstoves and WBTs which would help with the interpretation of the results.

Reply:

As mentioned in the manuscript (page 5, lines 116-118; page 7, lines 151-152), the OC and EC emissions, as well as the absorption of methanol extractable OC from cookstove combustions were reported in our previous work (Xie et al., 2018). In that study, the measurement data of modified combustion efficiency (MCE), overall thermal efficiency (OTE) and emission factors (EFs) of OC and EC for each fuel-cookstove combination were provided in supplementary information.

To make the results of this study comparable to field measurements in the future, we added MCE data for each fuel-cookstove combination in Table S1.

"*Tables S1 and S2 summarized the measurement results of Q_f and Q_b, respectively, for each fuel-cookstove combination, including concentrations of carbon contents and light-absorbing properties of sample extracts. As the light absorption of BB BrC is expected to depend largely on burn conditions (Saleh et al., 2014; Pokhrel et al., 2016), the MCE and EC/OC ratio, two indicators of burn conditions, are also given in Table S1.*" (lines 160-165)

The descriptions of the cookstoves and WBT protocol were added when replying to comments 1a and 1b.

1a. The stoves are listed in tables in the supplement; however, they are not really discussed in the experimental section of the main paper. How are they different? Where are they used around the world?

Reply:

In our previous study (Xie et al., 2018), the light absorption of organic carbon emitted from burning red oak wood and charcoal in cookstoves were investigated using the same samples as this work. That study also provided modified combustion efficiency (MCE) data, overall thermal efficiency (OTE), and emission factors (EFs) of OC and EC for each fuel-cookstove combination during high power phases of the water boiling test, showing the difference across fuel-specific cookstoves.

In the revised manuscript, we added a brief description of each fuel-specific cookstove in supplementary information (Text S1).

"*A brief description of each fuel-specific cookstove was given in supplementary information (Text S1)*" (Lines 141–142)

1b. Please include more information about the water boiling tests in the experimental section, as most readers of the journal will not be familiar with it. You should also mention the simmer phase is included for the hot start sample in some tests, if this is correct.

Reply:

In the revised manuscript, we added more information on the three test phases in the experimental section.

"*Both CS and HS phases are defined by the duration between the ignition and the water boils. The CS phase starts with the cookstove, pot, and water at ambient temperature; the HS immediately follows the CS with the cookstove hot but the pot and water at ambient temperature; and the SIM phase is defined by a 30-min time period with the cookstove hot and water temperature maintained at 3 ^{o}C below the boiling point.*" (lines 134-139)

The emission test of each fuel-cookstove combination contained a simmer (SIM) phase. Except the 3-stone fire, emission factors (EFs) of OC and EC at the SIM phase were substantially lower than those at high power phases (CS and HS) (Xie et al., 2018). Then, BrC absorption and its molecular composition were primarily measured for CS- and HS-phase samples. In the current work, the SIM-phase samples were analyzed only for red oak burning in a 3-stone fire. This test had comparable OC emissions between CS- and SIM-phase combustions (Xie et al., 2018), and the CS and HS phases of the 3-stone fire are typically similar and cannot be separated. The three SIM-phase samples from the 3-stone fire were treated as HS-phase samples of other cookstove tests. These information on sample selection were originally provided in supplementary information of the manuscript. To make it clear, we moved the information on sample selection to the experiment section of the main text.

"*Details for determinations of OCEC concentrations and BrC absorption were provided in supplementary information (Text S2). Except the 3-stone fire, EFs of OC and EC at the SIM phase were substantially lower than those at high power phases (CS and HS), so the BrC absorption from red oak and charcoal burning were primarily measured for CS- and HS-phase samples in Xie et al. (2018). The SIM-phase samples were analyzed only for red oak burning in a 3-stone fire. This test had comparable OC emissions between CS- and SIM-phase combustions, and CS and HS phases of the 3-stone fire were typically similar and could not be separated (Xie et al., 2018). In the current work, the same emission samples were selected for the analysis of NACs, and the three SIM-phase samples from the 3-stone fire were treated as HS-phase samples of other cookstove tests.*" (Lines 151-160)

1c. Could use more reasoning as to how red oak and charcoal are different as seen in Figure S1 C and F by relating hot start and cold start phases to the observed types of combustion. For example, hot start is mostly smoldering for charcoal (high OC emissions with very low BC and therefore low NOx to make less NACs).

Reply:

Thanks for the reviewer's suggestions.

In Table S1, the MCE values of charcoal burning indicate that the HS-phase burning is more smoldering than the CS-phase burning. However, the mass ratio of total NACs to OC in percentages ($tNAC_{OC}$%) showed no significant difference (p = 0.29) between HS and CS phases. Considering that the EC/OC ratio of charcoal burning was more sensitive to the initial temperature in the cookstove than MCE variations, it could not be used to predict burn conditions, BrC absorption, or NACs formation from charcoal burning.

Figure S1c and f are used to illustrate the dependence of NACs formation on burn conditions for red oak and charcoal combustions, respectively. Unlike biomass burning, the EC/OC ratio might not be used to parameterize burn conditions of charcoal in cookstoves. We provided a preliminary explanation on the difference of $tNAC_{OC}$% between red oak and charcoal combustions in lines 221-224.

"*Wood burning generates more volatile aromatic compounds (e.g., phenols, PAHs) than charcoal burning (Kim Oanh, et al., 1999), and NACs can form when aromatic compounds and reactive nitrogen (e.g., NO_X) are present during solid fuel combustion (Lin et al., 2016, 2017).*"

In comparison to red oak burning, charcoal combustion was more smoldering with significant smaller MCE values (p < 0.01). The wood fire tends to have reduced emissions of NO_X from the smoldering phase (Bertschi et al., 2003). But charcoal and wood are different fuels, and the emission factors (EFs) of NO_X were not measured for controlled cookstove tests in this work. Bhattacharya et al. (2002) reported the EFs of NO_X from a number of traditional and improved cookstoves. They found that EFs for NO_X using wood was slightly lower than charcoal. Then we might not infer that the charcoal burning should emit less NO_X to form NACs in this work.

In the revised manuscript, the original expression

"*Like MAC_{365} and $Å_{abs}$ in Q_f samples for charcoal burning (Xie et al., 2018), $tNAC_{OC}$% derived from the same samples did not correlate with EC/OC ratios in this work (Fig. S1f). Xie et al. (2018) found that the HS-phase for charcoal burning had average OC EFs 5–10 times higher than the CS-phase, while the EC EFs decreased by more than 90% from the CS- to HS-phase, so the EC/OC for charcoal burning is sensitive to the initial temperature in the cookstove, and cannot be used to predict burn conditions, BrC absorption, or NACs formation.*" (lines 253-258)

has been changed into

"*In Table S1, the MCE values of charcoal burning indicate that the HS-phase is more smoldering than the CS-phase. However, the average $tNAC_{OC}$% values showed no significant difference (p = 0.29) between HS and CS phases. Like MAC_{365} and $Å_{abs}$ in Q_f samples for charcoal burning (Xie et al., 2018), $tNAC_{OC}$% derived from the same samples did not correlate with EC/OC ratios in this work (Fig. S1f). Xie et al. (2018) found that the HS-phase for charcoal burning had average OC EFs 5–10 times higher than the CS-phase, while the EC EFs decreased by more than 90% from the CS- to HS-phase. Furthermore, no correlation has been observed between MCE and EC/OC for charcoal burning at the HS-phase. So, the EC/OC for charcoal burning tends to depend more on the initial temperature in the cookstove than MCE variations, and cannot be used to predict burn conditions, BrC absorption, or NACs formation.*" (lines 276-285)

2. Regarding source apportionment for NAC measurements (Lines 385-402), these fractions of NAC/OM will be very different in the field because OM can come from many sources. The NAC should be ratioed to a combustion product such as CO or EC.

Reply:

In the original manuscript, Figure 2 presents mass fraction patterns of individual NACs in OM from cookstove combustions using red oak wood and charcoal, open biomass burning, and photochemical reactions of typical aromatic precursors with NO_X. Receptor models are commonly used for source apportionment of particulate pollutants in the atmosphere (Jaeckels et al., 2007; Shrivastava et al., 2007; Xie et al., 2013), and assume that the ambient pollutants measured in the field are linear combinations from a number of time-variant sources/factors. When using field measurement data of NACs for receptor modeling, the resulting factors can be linked with specific emission sources by comparing with the NAC patterns shown in Figure 2 of this work. Further studies are warranted to unveil NACs patterns of other potential sources (e.g., motor vehicle emissions).

As we mentioned in the introduction, besides combustion sources, atmospheric NACs can also be generated through secondary pathways (lines 106-107). EC is specifically related to primary combustion sources, and CO is totally in the gas phase. In the current work, the gas-phase concentrations of NACs were not available.

To clarify the application of NAC patterns in source apportionment, we added some statement in lines 419-420 and 434-437.

"*This difference among NACs may help with source apportionment using receptor models, which are commonly used and assume that the ambient pollutants measured in the field are linear combinations from a number of time-variant sources/factors. (Jaeckels et al., 2007; Shrivastava et al., 2007; Xie et al., 2013).*"

"*When using field measurement data of NACs for receptor modeling, the resulting factors can be linked with specific emission sources by comparing with the NAC patterns shown in Fig. 2. Further studies are also warranted to unveil NAC patterns of other potential sources (e.g., motor vehicle emissions).*"

3. It is implied in lines 412-420 that NACs identified in this study are not significant BrC chromophores, however, if the quartz filter (Qb) is included the fraction is likely higher. It may be more appropriate to give an upper limit given that NACs on Qb could partition into the particle phase in the atmosphere. It is difficult to conclude that NACs are not significant BrC chromophores given the measurements on the sampling artifact that other studies have not considered. Also, NACs may be higher for fuel/stove/cooking activity combinations that result in more flaming combustion which produces NOx, an important reactant for NAC formation. Another factor is that the fractional absorption by NACs was not directly measured. Surrogates were used to quantify NAC concentrations and approximate MACs were used to calculate the Abs365.

Reply:

In the manuscript, we mentioned that most identified NACs are strong BrC chromophores, as the average contributions of total NACs to Abs_{365} of sample extracts were more than one order of magnitude higher than their average mass contributions.

"*The average contributions of total NACs to Abs_{365} ($Abs_{365,tNAC}$%) of the sample extracts (Q_f 1.10 – 2.57%, Q_b 10.7 – 21.0%) are up to 10 times greater than their average $tNAC_{OC}$% (Q_f 0.31 – 1.01%, Q_b 1.08 – 3.31%, Table 1). Considering that some NACs are not light-absorbing (Table S4) and the OM/OC ratio is typically greater than*

unity, most NACs that contribute to Abs_{365} are strong BrC chromophores." (Lines 446-450)

Due to the lack of authentic standards, the quantification of NACs concentrations and their contributions to Abs_{365} of Q_f extracts are subject to uncertainties. However, there are evidences showing that BrC absorption is majorly contributed by large molecules with MW > 500 – 1000 Da (Di Lorenzo and Young, 2016; Di Lorenzo et al., 2017). Large NACs molecules may be generated from cookstoves with flaming combustions, and their structures and light absorption are worth future investigations. In previous studies on ambient and biomass burning particles, most identified NACs had a MW lower than 300 – 500 Da, and their total contributions to bulk BrC absorption were estimated to be less than 10% (Mohr et al., 2013; Zhang et al., 2013; Teich et al., 2017; Xie et al., 2019). Similar results were also obtained in the current work. Even if the identified NACs on Q_b are totally derived from evaporation of the upstream filter (negative artifact), the adjusted average contributions of total NACs (Q_f + Q_b) to Abs_{365} of Q_f extracts are still lower than 5% (1.59 – 4.01%). Therefore, we suggest that further studies are needed to identify large BrC molecules (including high MW NACs) in ambient and source particles.

The original text from lines 412 to 420 has been changed into

"*All identified NACs explained 1.10 – 2.58% (Fig. S3) of Q_f extracts absorption. Even if the NACs on Q_b were totally derived from upstream filter evaporation, the adjusted average contributions of total NACs (Q_f + Q_b) to Abs_{365} of Q_f extracts were still lower than 5% (1.59 – 4.01%). Due to the lack of authentic standards, the quantification of NACs concentrations and their contributions to Abs_{365} of Q_f extracts might be subject to uncertainties. However, growing evidences showed that BrC absorption was majorly contributed by large molecules with MW > 500 – 1000 Da (Di Lorenzo and Young, 2016; Di Lorenzo et al., 2017). Large molecules of NACs may be generated from flaming combustions in cookstoves, and their structures and light absorption are worth future investigations. In previous studies on ambient and biomass burning particles, most identified NACs had a MW lower than 300 – 500 Da, and their total contributions to bulk BrC absorption were estimated to be less than 10% (Mohr et al., 2013; Zhang et al., 2013; Teich et al., 2017; Xie et al., 2019). Similar results were also obtained in the current work. Therefore, further studies are needed to identify large BrC molecules (including high MW NACs) in ambient and source particles.* " (Lines 457-471)

4. It is assumed that because Abs365,tNAC% at 365 nm is 7-11 times higher on the quartz fiber backup filter, that NACs may be important light absorbers in the gas phase (lines 442, 425-429, 432-434). To claim this in the paper, more discussion and reasoning for should be given.

4a. Those on the backing filter are not necessarily in the gas phase in the natural environment. As you explain in the paper, there are both positive and negative artifacts and there is not likely a straightforward way of calculating what would be in the gas phase.

Reply:

Thanks for the reviewer's suggestions. As we mentioned in the original manuscript, the NACs on Q_b were contributed by both positive (gaseous adsorption) and negative (filter evaporation) sampling artifacts. However, the relative contributions

of positive and negative artifacts to Q_b measurements are unknown. Furthermore, gas-phase NACs were not collected using an upstream denuder or an adsorbent cartridge downstream of the filter, and future work is needed to understand the gas/particle distribution of NACs in the ambient and source emissions. Due to the lack of gas-phase NACs data, we overstated that gaseous NACs might be an important group of light-absorbing species in the atmosphere.

The conclusions on light absorption of gaseous NACs has been deleted. Section 3.4 has been reorganized as follows.

"*The average $Abs_{365,iNAC}$% values of Q_f and Q_b samples are presented by fuel type and WBT phase in the Fig. 3 stack plots, and experimental data for each fuel-cookstove are provided in Tables S11–S14. The average contributions of total NACs to Abs_{365} ($Abs_{365,tNAC}$%) of the sample extracts (Q_f 1.10 – 2.57%, Q_b 10.7 – 21.0%) are up to 10 times greater than their average $tNAC_{OC}$% (Q_f 0.31 – 1.01%, Q_b 1.08 – 3.31%, Table 1). Considering that some NACs are not light-absorbing (Table S4) and the OM/OC ratio is typically greater than unity, most NACs that contribute to Abs_{365} are strong BrC chromophores. Like the mass composition of NACs (Fig. 1), $C_{10}H_7NO_3$ (CS 0.24%, HS 0.43%) and $C_8H_9NO_5$ (CS 1.22%, HS 0.55%) were the major contributors to Abs_{365} for the Q_f samples collected during red oak and charcoal burning, respectively (Fig.3a). The average $Abs_{365,tNAC}$% of Q_b samples are 7.53 to 11.3 times higher than those of Q_f samples. Unlike the Q_f samples from red oak burning, $C_{10}H_{11}NO_5$ (CS 2.77%, HS 3.09%) has the highest average contribution to Abs_{365} for Q_b samples, followed by $C_{10}H_7NO_3$ (CS 1.96%, HS 1.32%) and $C_8H_9NO_5$ (CS 1.32%, HS 1.44%). While $C_8H_9NO_5$ dominated the contribution (CS 8.78%, HS 5.82%) to Abs_{365} for the Q_b samples from charcoal burning (Fig. 3b). All identified NACs explained 1.10 – 2.58% (Fig. S3) of Q_f extracts absorption. Even if the NACs on Q_b were totally derived from upstream filter evaporation, the adjusted average contributions of total NACs (Q_f + Q_b) to Abs_{365} of Q_f extracts were still lower than 5% (1.59 – 4.01%). Due to the lack of authentic standards, the quantification of NACs concentrations and their contributions to Abs_{365} of Q_f extracts might be subject to uncertainties. However, growing evidences showed that BrC absorption was majorly contributed by large molecules with MW > 500 – 1000 Da (Di Lorenzo and Young, 2016; Di Lorenzo et al., 2017). Large molecules of NACs may be generated from flaming combustions in cookstoves, and their structures and light absorption are worth future investigations. In previous studies on ambient and biomass burning particles, most identified NACs had a MW lower than 300 – 500 Da, and their total contributions to bulk BrC absorption were estimated to be less than 10% (Mohr et al., 2013; Zhang et al., 2013; Teich et al., 2017; Xie et al., 2019). Similar results were also obtained in the current work. Therefore, further studies are needed to identify large BrC molecules (including high MW NACs) in ambient and source particles.* " (Lines 444-471)

4b. The vapor pressures of these molecules are very low, and the fraction in the gas phase is low. However, for some nitroaromatics such as 2-nitropenol the vapor pressure is higher. Are the concentrations for some molecules higher on the back up filter compared to the front filter and do we expect them to have higher vapor pressures?

Reply:

Due to the lack of measurement data of gas-phase NACs, the gas-phase fractions of NACs are unknown. 4-Nitrophenol (not 2-nitrophenol) was identified and quantified using authentic standards in this work. As the vapor pressure of NACs were rarely

measured or estimated in literatures, the Toxicity Estimation Software Tool (T.E.S.T) developed by the United States Environmental Protection Agency (US EPA) was used to predict subcooled vapor pressure of selected NACs standards at 25 ^{o}C ($p^{o,*}_{L}$) in the following Table.

Standard compounds	Formula	*m/z*, $[M-H]^-$	Vapor pressure (atm)
4-Nitrophenol	$C_6H_5NO_3$	138.0196	1.58×10^{-5}
2-Methyl-4-nitrophenol	$C_7H_7NO_3$	152.0353	4.57×10^{-6}
4-Nitrocatechol	$C_6H_5NO_4$	154.0145	3.37×10^{-7}
2-Methyl-5-nitrobenzoic acid	$C_8H_7NO_4$	180.0302	1.07×10^{-8}
2-Nitro-1-naphthol	$C_{10}H_7NO_3$	188.0353	4.62×10^{-8}

In comparison to the vapor pressure of *n*-alkanes and polycyclic aromatic hydrocarbons (PAHs) predicted by Xie et al. (2103, 2014), NACs listed in the above table are mostly more volatile than henicosane and fluoranthene (~10^{-8} atm). Xie et al. (2014) found that the gas-phase concentrations of *n*-alkanes and PAHs with vapor pressure greater than henicosane and fluoranthene were comparable or higher than their particle-phase concentrations. Furthermore, the average Q_b to Q_f mass ratios of the 17 individual NACs ranged from 54.3 ± 24.5% to 135 ± 52.4%, comparable to *n*-alkanes with carbon number ≤ 21 (e.g., henicosane; 26.3 – 163%) and PAHs with benzene ring number ≤ 4 (e.g., fluoranthene; 46.3 – 134%) in the ambient (Xie et al., 2014). So, we suspect that the identified NACs in this study may have substantial fractions remaining in the gas-phase.

In the revised manuscript, more discussions on NACs volatility were added in the last paragraph of section 3.2.

"*In this work, the average Q_b to Q_f mass ratios of the 17 individual NACs ranged from 50.8 ± 13.4% to 140 ± 52.9%, comparable to n-alkanes with carbon number ≤ 21 (e.g., henicosane; 26.3 – 163%) and PAHs with benzene ring number ≤ 4 (e.g., fluoranthene; 46.3 – 134%) in the ambient of urban Denver (Xie et al., 2014). Xie et al. (2014) found that the gas-phase concentrations of n-alkanes and PAHs with vapor pressure greater than henicosane and fluoranthene were comparable or higher than their particle-phase concentrations. The vapor pressure of five NACs standards at 25 ^{o}C ($p^{o,*}_{L}$) were predicted using the US EPA Toxicity Estimation Software Tool (T.E.S.T) and listed in Table S10. Their $p^{o,*}_{L}$ values are mostly higher than henicosane and fluoranthene (~10^{-8} atm; Xie et al., 2013, 2014). Then the identified NACs in this study may have substantial fractions remaining in the gas phase.*" Lines (332-341)

4c. What are the absorption cross sections for these molecules in the gas phase and their expected gaseous concentrations that would lead us to believe they are significant? Are they long-lived enough in the gas phase to be important? Only solution phase MACs at 365 nm are used to claim that gas phase absorption is significant and this is not sufficient.

Reply:

Thanks for the reviewer's comments.

In the current work, NACs from cookstove emissions were identified and quantified using filter samples only. The gas-phase concentrations, absorption cross sections, and life times of identified NACs were not measured or predicted. So, we

overstated that gaseous NACs might be an important group of light-absorbing species in the atmosphere. The conclusions on light absorption of gaseous NACs has been deleted.

5. Line 132: Omit that you did kerosene tests. It is not critical as you do not discuss these results.

Reply:

The expression in the method section has been changed as suggested. We omitted kerosene tests.

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Zhang, X., Lin, Y.-H., Surratt, J. D., and Weber, R. J.: Sources, Composition and Absorption Ångström Exponent of Light-absorbing Organic Components in Aerosol Extracts from the Los Angeles Basin, Environmental Science & Technology, 47, 3685-3693, 10.1021/es305047b, 2013.

Reviewer 2

This manuscript presents the analysis of N-containing aromatic compounds (NAC) in PM2.5 samples collected from biomass-burning emissions of wood and charcoal in special household stoves. Prior to the HPLC analysis, the collected filters were spiked with one deuterated internal standard and extracted in methanol. The goal of this research was to estimate the contribution of BrC NAC species to the total absorption of PM2.5 samples. The authors also discussed the differences (in OC, total NAC, individual NACs, etc.) between the hot-start and cold-start phases, and also between front and back filters. The authors acknowledged the limitations of this study (e.g., no gas-phase NACs were measured). This study is scientifically important, since NACs are not only light-absorbing compounds, but also are toxic organic species and they are still not well characterized. The manuscript is well organized and well written. I have a few major comments. In summary, I recommend this manuscript for publication after major revisions

Reply:

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

Major comments:

1. The filter samples were spiked with only one deuterated I.S. compound (4-nitrophenol-d4, C6), while the analyzed NACs (Fig 1) have different volatility levels (C7-C11). The author should check if there were potential losses of I.S., which is more volatile than the rest of the analyzed species, and if these losses led to a large overestimates of the concentrations of the analyzed compounds.

Reply:

In this study, the NACs in filter samples were determined identically as Xie et al. (2017, 2019). To minimize the evaporation loss, the sample extract volume was reduced using rotary evaporator under a vacuum, but not nitrogen blowdown evaporation. The coefficient of variation (CV) of the peak area for internal standard (IS) was only 0.16, indicating a stable IS signal. In addition, method recoveries were determined by spiking blank filters with known amounts of standard compounds, followed by extraction and quantification in the same way as that for collected samples. At the end of section 2.2, we mentioned that the average recoveries of NAC standards on pre-baked blank filters ranged from 75.1% to 116% (Lines 197-198). Therefore, the measurement results were not subject to uncertainties due to the loss of internal standard.

2. The manuscript contains a lot of abbreviations, which made it very hard to read (HS, CS, Qf, Qb, WBT, OMMs, SIM, etc.)

Reply:

We have defined each abbreviation in the abstract and the rest of the text at the first instance, which satisfied the requirement of the journal.

3. Table 1. The concentrations of the total NACs are strikingly high for the backup filters. I am wondering if some sort of unexpected breakthrough happened during the

sampling (especially in the case of charcoal burning). Would it be possible that the BB emissions were quite hot during the sampling, which caused the evaporation from the front filter?

Reply:

The mass concentrations of OC and EC were measured for the same filter samples in our previous work (Xie et al., 2018). As no EC has been detected on backup filters (Q_b), the breakthrough of particles was not expected during the sampling.

As shown in Table S2, filter samples were mostly collected at ambient temperature (~25 ^oC). We suspect that the identified NACs in this work have substantial fractions remaining in the gas phase (Lines 332-341).

In lines 344-347, we mentioned that the filter samples were mostly collected near ambient temperature.

"*Considering that most of the Q_f and Q_b samples were collected near ambient temperature (Table S2, ~25 ^oC), the composition of NACs derived from Q_f measurements alone can be biased due to the lack of gas-phase measurements.*"

4. Some minor comments Line 130. U.S. EPA – please make sure abbreviations are explained in the text Line 131: "USA" should be added after "NC" Line 126, what is "Jiko Poa"? Should company name be added? Lines 152, 156 etc. Company name (+city, state, country) of material and instruments is missing.

Reply:

In the revised manuscript, we defined US EPA before it first appeared (Lines 128-129).

"USA" was added after "NC" in line 130.

We added a brief description for all cookstoves, including "Jiko Poa", in supplementary information (Text S1). The company and country names (BURN Manufacturing, Kenya) were added right after "Jiko Poa" (Line 141).

Company, state, and country were added for materials and instruments in lines 169-170, 173.

References

Xie, M., Chen, X., Hays, M. D., Lewandowski, M., Offenberg, J., Kleindienst, T. E., and Holder, A. L.: Light Absorption of Secondary Organic Aerosol: Composition and Contribution of Nitroaromatic Compounds, Environmental Science & Technology, 51, 11607-11616, 10.1021/acs.est.7b03263, 2017.

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.

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)

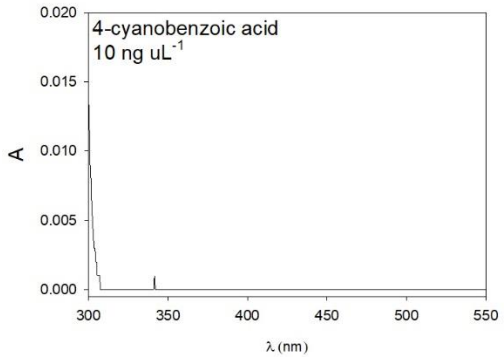
4. Line 283: In Table S3, the authors suggest C8H5NO2 as 3-cyanobenzoic acid. This is commercially available from several chemical suppliers, and it can be positively identified if C8H5NO2 correspond to the authors' suggestion. I ask the authors to purchase the standard compound and quantify it instead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

Chemical composition, structures, and light absorption of N-containing aromatic compounds emitted from burning wood and charcoal in household cookstoves

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Abstract

N-containing aromatic compounds (NACs) are an important group of light-absorbing molecules in the atmosphere. They are often observed in combustion emissions, but their chemical formulas and structural characteristics remain uncertain. In this study, red oak wood and charcoal fuels were burned in cookstoves using the standard water boiling test (WBT) procedure. Submicron aerosol particles in the cookstove emissions were collected using quartz (Q_f) and polytetrafluoroethylene (PTFE) filter membranes positioned in parallel. A back-up quartz filter (Q_b) was also installed downstream of the PTFE filter to evaluate the effect of sampling artifact on NACs measurements. Liquid chromatography-mass spectroscopy (LC-MS) techniques identified seventeen NAC chemical formulas in the cookstove emissions. The average concentrations of total NACs in Q_b samples (0.37 ± 0.31 – 1.7~~89~~ ± 0.7~~87~~ μg m^{-3}) were greater than 50% of those observed in the Q_f samples (0.~~47~~51 ± 0.4~~03~~ – 3.~~54~~91 ± ~~1.63~~2.06 μg m^{-3}), and the Q_b to Q_f mass ratios of individual NACs had a range of 0.02 – 2.71, indicating that the identified NACs might have substantial fractions remaining in the gas-phase. In comparison to other sources, cookstove emissions from red oak or charcoal fuels did not exhibit unique NAC structural features, but had distinct NACs composition. However, before identifying NACs sources by combining their structural and compositional information, the gas-particle partitioning behaviors of NACs should be further investigated. The average contributions of total NACs to the light absorption of organic matter at λ = 365 nm (1.10 – 2.5~~87~~%) in Q_f ~~samples are much lower than those in~~and Q_b samples (10.7 – 21.0%) are up to 10 times larger than their mass contributions (Q_f 0.31 – 1.01%, Q_b 1.08 – 3.31%), so the identified NACs are mostly strong light absorbers. To explain more sample extracts absorption, ~~These results suggest that more research~~future research is needed to understand the chemical and optical properties of ~~gaseous chromophores and heavier~~high molecular weight (e.g., MW > 500 Da) entities in particulate matter.

1 Introduction

In the developing world, 2.8 billion people burn solid fuels in household cookstoves for domestic activities such as heating and cooking (Bonjour et al., 2013). A variety of gaseous and ~~particulate~~ particle-phase pollutants ── carbon monoxide (CO), nitrogen oxides (NO_X), volatile organic compounds (VOCs), fine particulate matter with aerodynamic diameter ≤ 2.5 μm ($PM_{2.5}$), black carbon (BC), organic carbon (OC), etc. ── are emitted from cookstoves largely due to incomplete combustion (Jetter et al., 2012; Shen et al., 2012; Wathore et al., 2017). In China, the relative contributions of residential coal and biomass burning (BB) to annual $PM_{2.5}$ emissions decreased from 47% (4.32 Tg) in 1990 to 34% (4.39 Tg) in 2005 due to the growth in industrial emissions (Lei et al., 2011). Although, more than half of BC (> 50 %) and OC (> 60 %) emissions are attributed to residential coal and BB in both China and India (Cao et al., 2006; Klimont et al., 2009; Lei et al., 2011).

Household solid fuel combustion is a leading human health risk, especially for women and children who tend to spend more time indoors than men (Anenberg et al., 2013). Estimates show that exposures to $PM_{2.5}$ from domestic solid fuel combustion caused 3.9 million premature deaths and ~4.8% of lost healthy life years (Smith et al., 2014). In addition, the emissions of carbonaceous aerosols from cookstoves can affect the Earth's radiative balance by absorbing and scattering incoming solar radiation (Lacey and Henze, 2015; Aunan et al., 2009). BC is the most efficient light absorber in the atmosphere, while the total aerosol absorption, including that from OC, is still highly uncertain (Yang et al.,2009; Park et al., 2010; Feng et al., 2013; Wang et al., 2014; Tuccella et al., 2020). Multiple field and laboratory studies have demonstrated that OC in both primary PM emissions (e.g., biomass and fossil fuel combustions) and secondary organic aerosol (SOA) feature

a range of absorptivity in the near ultraviolet (UV) and short visible wavelength regions (Nakayama et al., 2010; Forrister et al., 2015; Lin et al., 2015; De Haan et al., 2017; Xie et al., 2017a, b, 2018). The light absorbing OC fraction is often referred to as "brown carbon" (BrC). Unlike open BB (e.g., forest, grassland, and cropland fires) ── one of the most important primary sources for organic aerosols (Bond et al., 2004) ── the light absorption of BrC from household cookstove emissions is rarely investigated. Sun et al. (2017) found that the BrC absorption from residential coal burning accounted for 26.5% of the total aerosol absorption at 350~850 nm. BrC from wood combustion in cookstoves has a greater mass specific absorption than that from open BB over the wavelength range of 300 – 550 nm (Xie et al., 2018). These results suggest that cookstove emissions may also be an important BrC source, which needs to be accounted for separately from open BB.

Organic molecular markers (OMMs) are commonly used in receptor-based source apportionment of carbonaceous aerosols (Jaeckels et al., 2007; Shrivastava et al., 2007; Xie et al., 2012). Polycyclic aromatic hydrocarbons (PAHs) and their derivatives are a group of OMMs with light absorption properties dependent on ring number or the degree of conjugation (Samburova et al., 2016). As discussed in Xie et al. (2019), PAHs are generated from a multitude of combustion processes (e.g., BB, fossil fuel combustion) (Chen et al., 2005; Riddle et al., 2007; Samburova et al., 2016), and their ubiquitous nature makes them less than ideal OMMs for BrC source attribution. Because of the specific toxicological concern raised by PAHs ── they are mutagenic and carcinogenic [International Agency for Research on Cancer (IARC), 2010] ── source emission factors (EFs), ambient levels, and potential health effects of PAHs are investigated exhaustively (Ravindra et al., 2008; Kim et al., 2013). Similar to PAHs, N-containing aromatic compounds (NACs) are a group of BrC chromophores commonly detected in ambient PM and source

emissions. Zhang et al. (2013) and Teich et al. (2017) calculated the absorption of individual NACs in aqueous extracts of ambient PM, the total of which explained ~3% of the bulk extract absorption at 365 – 370 nm. With the same approach, Xie et al. (2017a, 2019) found that the absorbance due to NACs in BB or secondary OC was 3 – 10 times higher than their mass contributions. Lin et al. (2016, 2017) estimated an absorbance contribution of 50 – 80% from NACs in BB OC directly from their high-performance liquid chromatography (HPLC)/photodiode array (PDA) signals, which are subject to considerable uncertainty due to the co-elution of other BrC chromophores (e.g., PAHs and their derivatives). These results indicate that NACs are strong BrC chromophores, but the estimation of their contributions to BrC absorption depends largely on how well they are chemically characterized. Nitrophenols, methyl nitrophenols, nitrocatechols and methyl nitrocatechols (including isomers) are typical atmospheric NACs (Claeys et al., 2012; Desyaterik et al., 2013; Zhang et al., 2013). These NACs can be generated from BB (Lin et al., 2016, 2017; Xie et al., 2019), fossil fuel combustion (Lu et al., 2019), and the reactions of aromatic volatile organic compounds (VOCs) with reactive nitrogen species (e.g., NO_X) (Xie et al., 2017a), and are not unique to specific sources (e.g., BB). By using a HPLC interfaced to a diode array detector (DAD) and quadrupole (Q) time-of-flight mass spectrometer (ToF-MS), Xie et al. (2019) found that BB NACs contain methoxy and cyanate groups. Nitronaphthol, nitrobenzenetriol, and methyl nitrobenzenetriol are characteristic NACs for NO_X-based chamber reactions of naphthalene, benzene, and *m*-cresol, respectively (Xie et al., 2017a). Yet, few studies have investigated the composition of NACs from household cookstove emissions (Fleming et al., 2018; Lu et al., 2019).

The present study aims to characterize NACs in $PM_{2.5}$ from burning red oak and charcoal in a variety of cookstoves and calculate their contributions to bulk OC absorption. The absorption of OC in solvent extracts of cookstove emissions were measured in our previous work (Xie et al.,

2018). Presently, NACs are identified and quantified using an earlier described HPLC/DAD-Q-ToF-MS system. In addition, the NACs adsorbed on a backup quartz filter downstream of a polytetrafluoroethylene (PTFE) membrane filter are analyzed, to evaluate the potential for sampling artifacts of $PM_{2.5}$ NACs ~~in $PM_{2.5}$~~ on the bare quartz filter in parallel. This work unveils BrC composition at a molecular level and increases the understanding of BrC chromophores and their sources. It also shows that further identification of large molecules (e.g., > 500 Da) may better explain BrC absorption in the particle phase ~~and that understanding the light absorption of gaseous chromophores is important for the future~~.

2 Methods

2.1. Cookstove emissions sampling

~~Details of t~~The cookstove emission test facility, fuel-cookstove combinations, water boiling test (WBT) protocol, and $PM_{2.5}$ emissions sampling were described previously in Jetter and Kariher (2009) and Jetter et al. (2012) ~~and Xie et al. (2018)~~. Briefly, the cookstove emission~~s~~ tests were performed at the United States Environmental Protection Agency (U~~.~~S~~.~~ EPA) cookstove test facility in Research Triangle Park, NC, USA. ~~Three fuels (R~~red oak wood~~,~~ and lump charcoal~~, and 1-K kerosene)~~ were burned in fuel-specific cookstoves under controlled conditions. Emissions tests for each fuel-cookstove combination were performed in triplicate. The WBT protocol (version 4) (Global Alliance for Clean Cookstoves, 2014) is designed to measure cookstove power, energy efficiency, and fuel use, and contains cold-start (CS) high power, hot-start (HS) high power, and simmer (SIM) low power phases. Both CS and HS phases are defined by the duration between the ignition and the water boils. The CS phase starts with the cookstove, pot, and water at ambient temperature; the HS immediately follows the CS with the cookstove hot but the pot and water at ambient temperature; and the SIM phase is defined by a 30-min time period with the cookstove

hot and water temperature maintained at 3 °C below the boiling point. ~~Due to the limited sample number (n = 6) and low OC emissions from kerosene burning, only red oak and charcoal burning samples were used for NACs analysis.~~ Low moisture (~10%) oak and charcoal fuels were burned with five specific-designed cookstove types (Tables S1 and S2); high moisture (~30%) oak fuels were burned in one cookstove (Jiko Poa, BURN Manufacturing, Kenya). A brief description of each fuel-specific cookstove was given in supplementary information (Text S1). ~~Emissions tests for each fuel-cookstove combination were performed in triplicate. The WBT protocol (version 4) (Global Alliance for Clean Cookstoves, 2014) is designed to measure cookstove power, energy efficiency and fuel use and utilizes cold-start (CS) high power, hot-start (HS) high power, and simmer (SIM) low power phases.~~ Gaseous pollutant (e.g., CO, methane (CH_4)) emissions were monitored continuously, and $PM_{2.5}$ filter samples were collected during each test phase of the WBT protocol. The modified combustion efficiency (MCE), defined as $CO_2/(CO_2 + CO)$ on a molar basis, was calculated and discussed in Xie et al. (2018). A quartz-fiber filter (Q_f) and a PTFE membrane filter positioned in parallel collected $PM_{2.5}$ isokinetically at a flow rate of 16.7 L min^{-1}. The ~~A~~adsorption artifact of Q_f was evaluated using a quartz-fiber back-up filter (Q_b) installed downstream of the PTFE filter during $PM_{2.5}$ sampling.

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2.2. Chemical analysis

The OC and elemental carbon (EC) emissions and UV-Vis light absorption properties (BrC) of methanol-extracted cookstove particles were reported in Xie et al. (2018). Details ~~of~~ for ~~the method~~determinations of OCEC concentrations and BrC absorption ~~, sample selection~~were provided in supplementary information (Text S2). Except the 3-stone fire, EFs of OC and EC at the SIM phase were substantially lower than those at high power phases (CS and HS), so the BrC absorption from red oak and charcoal burning were primarily measured for CS- and HS-phase

samples in Xie et al. (2018). The SIM-phase samples were analyzed only for red oak burning in a 3-stone fire. This test had comparable OC emissions between CS- and SIM-phase combustions, and CS and HS phases of the 3-stone fire were typically similar and could not be separated (Xie et al., 2018). In the current work, the same emission samples were selected for the analysis of NACs, and the three SIM-phase samples from the 3-stone fire were treated as HS-phase samples of other cookstove tests. Tables S1 and S2 summarized the measurement results of Q_f and Q_b, respectively, for each fuel-cookstove combination, including concentrations of carbon contents and light-absorbing properties of sample extracts. As the light absorption of BB BrC is expected to depend largely on burn conditions (Saleh et al., 2014; Pokhrel et al., 2016), the MCE and EC/OC ratio, two indicators of burn conditions, are also given in Table S1.~~, and measurement results are summarized in supplementary information (Text S1, Tables S1 and S2).~~

The Q_f and Q_b sample extraction and subsequent analysis for NACs were conducted as described in Xie et al. (2019). In brief, an aliquot of each filter sample was pre-spiked with 250 ng nitrophenol-d4 (internal standard) and extracted ultrasonically twice for 15 min in 3-5 mL of methanol. After filtration (30 mm diameter~~.~~ ×0.2 μm pore size, PTFE filter, National Scientific Co. Ltd, TN, USA), the extract volume was reduced to ~500 μL with rotary evaporation prior to HPLC/DAD-MS (Q-ToF) analysis. The NACs targeted in this work were chromatographed using an Agilent 1200 Series HPLC equipped with a Zorbax Eclipse Plus C18 column (2.1 mm × 100 mm, 1.8 μm particle size; Agilent Technologies, CA, USA). The gradient separation was performed using water (eluent A) and methanol (eluent B) containing 0.2% acetic acid (v/v) with a total flow rate of 0.2 mL min^{-1}. The eluent B fraction was held at 25% for 3 min, increased to 100% over the next 7 min, where it was held for 22 min, and then returned to 25% over 5 min. An Agilent 6520 Q-ToF MS equipped with a multimode ion source operating in electrospray

ionization (ESI) negative (–) mode was used to determine the chemical formula, molecular weight (MW), and quantity of each target compound. All sample extracts were analyzed in full scan mode over 40–1000 Da. A mass accuracy of ± 10 ppm was selected for compound identification and quantification. Samples with individual NACs exhibiting the highest MS signal intensities in full scan mode were re-examined in targeted MS-MS mode using a collision-induced dissociation (CID) technique. The MS-MS spectra of target NACs $[M-H]^-$ ions were acquired to deduce structural information. Similar to bulk carbon and light absorption measurements, NACs were primarily determined for CS- and HS-phase samples with substantial OC loadings.

Due to the limited availability of authentic standards, many of the NACs identified in cookstove combustion samples were quantified using surrogate compounds with similar MW or structures. An internal standard method with a 9-point calibration curve (~0.01 – 2 ng μL^{-1}) was applied for quantification of concentrations. The compounds represented by each identified NAC formula were quantified individually and combined to calculate the mass ratio of total NACs to OC ($\mu g\ m^{-3}$) × 100% ($tNAC_{OC}$%). Presently, the organic matter (OM) to OC ratio was not measured or estimated for cookstove combustion emissions, so $tNAC_{OC}$% could be up to 2 times greater than the contributions of NACs to OM (Reff et al., 2009; Turpin and Lim, 2001). Table S3 lists the chemical formulas, proposed structures, and standard assignments for the NACs identified here. The quality assurance and control (QA/QC) procedures for filter extraction and instrumental analysis were the same as Xie et al. (2017a, 2019). NACs were not detected in field blank and background samples. The average recoveries of NAC standards on pre-spiked blank filters ranged from 75.1% to 116%, and the method detection limit had a range of 0.70–17.6 pg.

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2.3. Data analysis

In Xie et al. (2017a), the DAD measurement directly identified the chemical compounds in chamber SOA responsible for light absorption in the near UV and visible light ranges. However, no light absorption from individual NACs was detected in the DAD chromatograms from open BB (Xie et al., 2019) and cookstove emissions (this work). So the contributions of individual NACs to light absorption coefficient (Abs_{λ}, Mm^{-1}) for each sample extract at 365 nm ($Abs_{365,iNAC}$%) were calculated using the method described in Xie et al. (2017a, 2019):

$$Abs_{365,iNAC}\% = \frac{C_{iNAC} \times MAC_{365,iNAC}}{Abs_{365}} \times 100\% \quad (1)$$

where C_{iNAC} is the mass concentration (ng m^{-3}) of individual NACs, and $MAC_{365,iNAC}$ is the mass absorption coefficient (MAC_{λ}, $m^2\ g^{-1}$) of individual NACs at 365 nm. Abs_{365} is the light absorption coefficient (Mm^{-1}) of each sample extract at 365 nm, and has been widely used to represent BrC absorption (Chen and Bond, 2010; Hecobian et al., 2010; Liu et al., 2013). Each NAC compound was assumed to absorb as a standard (Table S3), of which the $MAC_{365,iNAC}$ value was obtained from Xie et al. (2017a, 2019) and listed in Table S4. In this work, Student's *t*-test was used to determine if the means of two sets of data are significantly different from each other, and a *p* value less than 0.05 indicates significant difference.

3 Results and discussion

3.1 Summary of total NACs concentration from cookstove emissions

Table 1 summarizes the average concentrations of total NACs and average $tNAC_{OC}$% for Q_f and Q_b by fuel type and WBT phase. The EFs of total NACs shown in Table S5 were obtained by multiplying the EFs of OC and $tNAC_{OC}$%. Filter samples of emissions from burning red oak wood ~~show~~ had significantly ($p < 0.05$) higher average total NAC concentrations and $tNAC_{OC}$% than the charcoal burning samples. Wood burning generates more volatile aromatic compounds (e.g., phenols, PAHs) than charcoal burning (Kim Oanh, et al., 1999), and NACs can form when

aromatic compounds and reactive nitrogen (e.g., NO_X) are present during solid fuel combustion (Lin et al., 2016, 2017). While burning red oak, emissions from the CS and HS phases show similar average NAC concentrations, ~~and~~ $tNAC_{OC}$%, and NAC EFs (Tables ~~–~~ 1 and S5). Additionally, burning low moisture red oak in the Jiko Poa stove had higher $tNAC_{OC}$% than burning high moisture red oak (Tables S6 and S7), but the difference was not significant ($p > 0.05$). ~~or high moisture red oak in the Jiko Poa stove shows no significant ($p > 0.05$) difference in $tNAC_{OC}$% (Tables S5 and S6).~~ Thus, the NAC ~~and OC~~ emissions from red oak burning are less likely influenced by WBT phase, and the effect of fuel moisture content needs further investigation ~~or fuel moisture~~. For charcoal fuel samples, compared with the CS-phase, the HS-phase shows significantly higher ($p < 0.05$) average NAC concentrations. This is likely due to the increase in OC with the HS phase (Tables 1 and S5~~Table 1~~), as the average $tNAC_{OC}$% values are much closer for the CS- (0.~~38~~ 40 ± 0.25%) and HS-phases (0.31 ± 0.~~22~~21%).

Several studies have placed a quartz-fiber filter behind a PTFE filter to evaluate the positive adsorption artifact — adsorption of gas-phase compounds onto particle filter media, "blow-on" effect (Peters et al., 2000; Subramanian et al., 2004; Watson et al., 2009; Xie et al., 2014). This method is expected to provide a consistent estimate irrespective of sampling time, but may over correct the positive artifact by 16–20% due to volatilization of OC off the upstream PTFE filter (negative artifact, "blow-off" effect) (Subramannian et al., 2004). 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). The present study is the first to consider sampling artifact when measuring semivolatile NACs. This concept merits consideration as

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quantification of particle-phase NACs may be subject to large uncertainty. Table 1 shows that the average concentrations of total NACs on Q_b (0.37 ± 0.31 – 1.~~78~~ 79 ± 0.~~78~~ 77 μg m^{-3}) are greater than ~~50~~50% and ~~70~~80% of those on Q_f (0.~~47~~ 51 ± 0.~~40~~ 43 – 3.~~54~~ 91 ± ~~1.63~~2.06 μg m^{-3}) for red oak and charcoal burning, respectively. The average Q_b to Q_f ratio in percentage using OC concentrations is 2-3 times lower (14.8 ± 3.87 – 38.8 ± 18.9%). Hence, the NACs identified in this work are present in the relatively volatile bulk OC fraction emitted from cookstoves, and the NACs in the Q_f samples may also be present in the gas-phase in the atmosphere. Charcoal burning emissions show even higher (p <0.05) Q_b to Q_f total NAC mass ratios (CS ~~87.7~~84.1 ± ~~34.2~~38.0%, HS ~~143~~ 140 ± ~~51.4~~52.9%) than red oak burning (CS ~~53.0~~50.8 ± ~~10.6~~13.4%, HS 5~~5.1~~3.4 ± ~~24.7~~26.2%), which is largely due to the higher OC loads on Q_f ~~samples~~ from red oak burning. Xie et al. (2018) assumed previously that the Q_b-adsorbed OC represented the positive sampling artifact only, and adjusted the light absorbing properties of OC on Q_f by subtracting Abs_{365} and OC of Q_b samples directly. In this study, the high Q_b to Q_f ratios of total NACs indicate that the volatilization of NACs from upstream PTFE filter cannot be neglected, but the relative contributions of positive and negative artifacts to Q_b measurements are unknown. Therefore, the measurement results of NACs in Q_f and Q_b samples were provided separately, and no correction was conducted for Q_f measurements in this work. Since the gaseous NACs adsorbed ~~on~~ in Q_b samples depends on Q_f loadings, $tNAC_{OC}$% and total NACs concentrations in each Q_f-Q_b pair from matching tests are significantly correlated (p < 0.05, Fig. S1a, b, d, and e).

Along with modified combustion efficiency (MCE), the EC/OC and BC/OA (organic aerosol) ratios were used previously as indicators of biomass burning conditions (McMeeking et al., 2014; Pokhrel et al., 2016). Here the burn condition indicates general flame intensity or combustion temperature (Chen and Bond, 2010; Saleh et al., 2014), and is parameterized to

investigate combustion processes (e.g., pyrolysis). The MCE, EC/OC and BC/OA ratios are key to understanding particulate OC absorptivity (Saleh et al., 2014; Lu et al., 2015) and NACs formation from open BB (Xie et al., 2019). Presently, the relationships of $tNAC_{OC}$% versus EC/OC for Q_f samples are shown in Fig. S1c and f by fuel type. Because no significant difference was observed for average total NACs concentrations, $tNAC_{OC}$%, and EC/OC ratios when testing CS- versus HS- phases during red oak fuel burning, the CS- and HS-phases were pooled for a regression analysis. The $tNAC_{OC}$% of Q_f samples positively correlate ($r = 0.83$, $p < 0.05$) with EC/OC for red oak burning (Fig. S1c), as observed in Xie et al. (2019) for open BB, which suggests that burn conditions influence NACs formation during BB. Note that the NAC concentrations on Q_f were possibly adsorbed while in a gaseous state, while EC is particle phase.

In Table S1, the MCE values of charcoal burning indicate that the HS-phase is more smoldering than the CS-phase. However, the average $tNAC_{OC}$% values showed no significant difference ($p = 0.29$) between HS and CS phases. Like MAC_{365} and $Å_{abs}$ in Q_f samples for charcoal burning (Xie et al., 2018), $tNAC_{OC}$% derived from the same samples did not correlate with EC/OC ratios in this work (Fig. S1f). Xie et al. (2018) found that the HS-phase for charcoal burning had average OC EFs 5–10 times higher than the CS-phase, while the EC EFs decreased by more than 90% from the CS- to HS-phase~~,~~. Furthermore, no correlation has been observed between MCE and EC/OC for charcoal burning at the HS-phase. ~~so~~So, the EC/OC for charcoal burning ~~is~~tends to depend ~~-~~more on ~~sensitive to~~ the initial temperature in the cookstove than MCE variations, and cannot be used to predict burn conditions, BrC absorption, or NACs formation.

3.2 Composition of NACs in Q_f and Q_b

During solid fuel combustion, NACs may form from aromatic compounds (e.g., substituted phenols) and reactive nitrogen species (e.g., NH_3, NO_X, and HONO) in both the gas- and particle-

phase (Harrison et al., 2005; Kwamena and Abbatt, 2008; Lu et al., 2011; Lin et al., 2016, 2017). Aromatic hydrocarbons are produced during fuel pyrolysis (Simoneit et al., 1993; Simoneit, 2002; Kaal et al., 2009). Oxidation of fuel derived nitrogen, rather than molecular nitrogen in air, is the major formation pathway of reactive nitrogen species (Glarborg et al., 2003).

Presently, seventeen chemical formulas were identified as NACs in cookstove emissions, several of which are widely observed in ambient air and open BB particles (e.g., $C_6H_5NO_3$, $C_6H_5NO_4$) (Claeys et al., 2012; Zhang et al., 2013; Lin et al., 2016, 2017; Xie et al., 2019). Figure 1 shows the average concentrations (ng m^{-3}) of individual NACs in Q_f and Q_b samples by fuel type and WBT phase. The corresponding average mass ratios of individual NACs to OC × 100% ($iNAC_{OC}$%) are ~~shown~~ exhibited in Fig. S2. Details of the NACs composition expressed in $iNAC_{OC}$% for each fuel-cookstove experiment are given in Tables ~~S5~~S6~~ S8~~S9.

Generally, the CS and HS phases have consistent NAC profiles for red oak combustion (Figs. 1a, b and S2a, b). $C_{10}H_7NO_3$ (CS-Q_f 1003 ± 803 ng m^{-3}, HS-Q_f 1149 ± 1053 ng m^{-3}) and $C_8H_5NO_2$ (CS-Q_f 712 ± 921 ng m^{-3}, HS-Q_f 1185 ± 1761 ng m^{-3}) ~~has~~ have the highest average concentrations ~~(CS-Q_f 1003 ± 803 ng m^{-3}, HS-Q_f 1149 ± 1053 ng m^{-3}) and $iNAC_{OC}$% (CS-Q_f 0.45 ± 0.80%, HS-Q_f 0.43 ± 0.79%)~~ on Q_f, followed by $C_{11}H_9NO_3$, $C_{10}H_{11}NO_5$, and $C_{11}H_{13}NO_5$. However, $C_8H_5NO_2$ was only detected in emission samples of Jiko Poa among the five wood stoves (Tables S6 and S7). Not considering $C_8H_5NO_2$, ~~–~~ Q_b samples of red oak combustion emissions have similar NACs profiles and characteristic species (e.g., $C_{10}H_7NO_3$, $C_{11}H_9NO_3$) as Q_f samples, and the individual NAC distributions in Q_b to Q_f samples are similar between the CS- and HS-phases (Fig. 1a, b). It appears that the formation of NACs from red oak burning in cookstoves depends largely on burn conditions reflected by EC/OC ratios (Fig. S1c) rather than WBT phases. Among the 17 identified NACs from red oak burning, $C_8H_5NO_2$ and $C_{11}H_{13}NO_6$

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have the lowest Q_b to Q_f ratios (2.~~42~~ 03 – ~~12.6~~9.80%, Fig. 1a, b), indicating their low volatility. The low volatility of $C_{11}H_{13}NO_6$ might be due to its relatively high MW; while $C_8H_5NO_2$ has the second lowest MW and its structure likely contains functional groups that decrease vapor pressure (e.g., carboxyl group) (Donahue et al., 2011).

Charcoal burning generated high abundances of $C_8H_9NO_5$, $C_{11}H_9NO_3$, and $C_{10}H_7NO_3$ for both CS (86.6 ± 98.7 – 170 ± 200 ng m^{-3}) and HS (97.1 ± 38.5 – 178 ± 104 ng m^{-3}) phases (Figs. 1c, d and S2c, d). Only one of the five charcoal stoves (Éclair, GIZ, Bonn, Germany) emitted $C_8H_5NO_2$, which was not detected on Q_b for charcoal combustions (Tables S8 and S9). Average concentrations of $C_8H_9NO_5$, $C_{11}H_9NO_3$, and $C_{10}H_7NO_3$ in the Q_b (62.0 ± 64.9 – 198 ± 115 ng m^{-3}) and Q_f samples were comparable. However, the $iNAC_{OC}$% of these compounds are 1.45 ± 0.68 – 5.16 ± 2.84 times higher in Q_b ($iNAC_{OC}$%, 0.11 ± 0.18 – 0.46 ± 0.69%) than in Q_f samples (0.052 ± 0.067 – 0.14 ± 0.15%). High levels of $C_6H_5NO_4$, $C_7H_7NO_4$, and $C_8H_9NO_4$ were also observed in the HS phase for charcoal burning (Fig. 1d). These compounds in Q_b samples had average concentrations (222 ± 132 – 297 ± 277 ng m^{-3}) 22.6 – 80.8% higher than in Q_f samples (150 ± 118 – 181 ± 111 ng m^{-3}). As such, the charcoal HS phase generates more low MW NACs (e.g., $C_6H_5NO_4$, $C_7H_7NO_4$) than the CS phase, and the initial temperature in the cookstove has an impact on NAC formation from charcoal burning.

As mentioned in section 3.1, using a Q_b has been widely applied to evaluate the positive sampling artifact for OC and semivolatile organic compounds. This method might only work for bulk PM, OC, and low volatile organic compounds, of which the concentrations in Q_b samples are much lower than Q_f samples and usually presumed to be due to positive adsorption artifacts only (Subramanian et al., 2004; Watson et al., 2009). In this work, the average Q_b to Q_f mass ratios of the 17 individual NACs ranged from ~~54.3~~50.8 ± ~~24.5~~13.4% to ~~135~~ 140 ± 52.~~4~~9%, comparable to

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n-alkanes with carbon number ≤ 21 (e.g., henicosane; 26.3 – 163%) and PAHs with benzene ring number ≤ 4 (e.g., fluoranthene; 46.3 – 134%) in the ambient of urban Denver (Xie et al., 2014). Xie et al. (2014) found that the gas-phase concentrations of *n*-alkanes and PAHs with vapor pressure greater than henicosane and fluoranthene were comparable or higher than their particle-phase concentrations. The vapor pressure of five NACs standards at 25 °C ($p^{o,*}_L$) were predicted using the US EPA Toxicity Estimation Software Tool (T.E.S.T) and listed in Table S10. Their $p^{o,*}_L$ values are mostly higher than henicosane and fluoranthene (~10^{-8} atm; Xie et al., 2013, 2014). Then the identified NACs in this study may have substantial fractions remaining in the gas phase. Asand the evaporation of NACs from Q_f the upstream filter (negative artifact) is unknown. As a result, the particle-phase NAC concentrations cannot be calculated by simply subtracting Q_b measurements from those of Q_f. Considering that most of the Q_f and Q_b samples were collected near ambient temperature (Table S2, ~25 °C), some of the identified NACs (e.g., 4-nitrophenol) may have substantial gas-phase concentrations (Li et al., 2020), and the composition of NACs derived from Q_f measurements alone can be biased due to the lack of gas-phase measurements. Future work is needed to evaluate the composition of NACs from emission sources in both the particle and gas phases.

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3.3 Identification of NACs structures

Figures S3 and S4 exhibited extracted ion chromatograms (EICs) and MS-MS spectra of the 17 identified NACs. For comparison, the MS-MS spectra of standard compounds used in this work are obtained from Xie et al. (2017a, 2019) and shown in Fig. S5. Among all identified NAC formulas, $C_{10}H_7NO_3$ was detected in each fuel-cookstove experiment (Tables S5 S6 – S8S9) and showed the highest concentrations in emissions from burning red oak (Fig. 1a, b). The MS-MS spectrum of $C_{10}H_7NO_3$ (Fig. S4l) is like 2-nitro-1-phenol (Fig. S5g) but shows a ~1 min difference

372 in retention time (Fig. S3i 10.9 min, 2-nitro-1-phenol 11.8 min). $C_{10}H_7NO_3$ is presumed to be an
373 isomer of 2-nitro-1-phenol with a nitronaphthol structure. $C_{11}H_9NO_3$ has a degree of unsaturation
374 and a fragmentation pattern (Fig. S4q) like $C_{10}H_7NO_3$ and is likely a structural isomer of methyl
375 nitronaphthol. $C_6H_5NO_3$, $C_7H_7NO_3$, $C_6H_5NO_4$, and $C_7H_7NO_4$ are commonly detected in
376 combustion emissions (Lin et al., 2016, 2017; Xie et al., ~~2017a~~2019) and atmospheric particles
377 (Claeys et al., 2012; Zhang et al., 2013). $C_6H_5NO_3$ and $C_6H_5NO_4$ are identified as 4-nitrophenol
378 and 4-nitrocatechol using authentic standards (Figs. S4a, d and S5a, c). $C_7H_7NO_3$ has two isomers
379 (Fig. S3b) and the compound eluting at 9.98 min has the same retention time and MS-MS spectrum
380 (Fig. S4c) as 2-methyl-4-nitrophenol (Fig. S5b). In ambient PM and chamber SOA, $C_7H_7NO_4$ was
381 identified using standard compounds as a series of methyl-nitrocatechol isomers (4-methyl-5-
382 nitrocatechol, 3-methyl-5-nitrocatechol, and 3-methyl-6-nitrocatechol) (Iinuma et al., 2010).
383 According to the HPLC-Q-ToFMS data for $C_7H_7NO_4$ identified in Iinuma et al. (2010) and our
384 previous studies (Xie et al., 2017a, 2019), the two $C_7H_7NO_4$ isomers in Fig. S3d are likely 4-
385 methyl-5-nitrocatechol and 3-methyl-6-nitrocatechol, respectively. Here we cannot rule out the
386 presence of 3-methyl-5-nitrocatechol, which may co-elute with 4-methyl-5-nitrocatechol (Iinuma
387 et al., 2010). In Fig. S4k, o, and p, the MS-MS spectra of $C_7H_7NO_5$, $C_8H_7NO_5$, and $C_8H_9NO_5$ all
388 show a loss of CH_3 + NO (or NO_2) + CO. The loss of CH_3 is typically due to a methoxy group in
389 NAC molecules, and NO (or NO_2) and CO loss is commonly observed for NACs with more than
390 one phenoxy group (Xie et al., 2019). So methoxy nitrophenol is the proposed skeleton for
391 $C_7H_7NO_5$, $C_8H_7NO_5$, and $C_8H_9NO_5$. Other functional groups were estimated using their chemical
392 formulas and degree of unsaturation as a basis (Table S3).

393 The present study quantifies $C_8H_7NO_4$ and $C_9H_9NO_4$ using 2-methyl-5-benzoic acid
394 ($C_8H_7NO_4$) and 2,5-dimethyl-4-nitrobenzoic acid ($C_9H_9NO_4$), respectively. The fragmentation

patterns of $C_8H_7NO_4$ (Fig. S4g, h) and $C_9H_9NO_4$ compounds (Fig. S4m, n) are different from their corresponding surrogates (Fig. S5f, h) and loss of CO_2 is not observed, so $C_8H_7NO_4$ and $C_9H_9NO_4$ compound structures do not include a carboxyl group. 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. However, the fragmentation mechanism related to the loss of a single nitrogen for the second $C_8H_7NO_4$ isomer (Figs. S3e~~, Fig.~~ and S4h) is unknown and requires further study. The MS-MS spectrum of the second $C_9H_9NO_4$ isomer had dominant ions at *m/z* 194 ($[M–H]^-$), 164 (loss of NO), and 149 (loss of NO + CH_3). Compared with the MS-MS spectra of 4-nitrophenol and 2-methyl-4-nitrophenol (Fig. S5a, b), the second $C_9H_9NO_4$ isomer is likely a methoxy nitrophenol with an extra ethyl group.

The EIC signal of $C_8H_9NO_4$ in Fig. S3f comprises at least 3-4 isomers, and the MS-MS spectra are always dominated by ions at m/z 182 ($[M–H]^-$), 152 (loss of NO), and 137 (loss of NO + CH_3) with some changes in relative abundance. The fragmentation mechanism of $C_8H_9NO_4$ represented by the MS-MS spectrum in Fig. S4i is consistent with that of the second $C_9H_9NO_4$ isomer (Fig. S4n), so the $C_8H_9NO_4$ might also have a methoxy nitrophenol skeleton.

~~Unlike other NACs, $C_8H_5NO_2$ was only detected in samples from red oak burning in the Jiko Poa and charcoal burning in the Éclair (Tables S5 – S8). The average mass ratios of $C_8H_5NO_2$ in Q_b to Q_f samples for red oak burning are less than 15% (CS phase 2.42%, HS phase 12.6%), and $C_8H_5NO_2$ was not detected in any Q_b samples for charcoal burning.~~ The MS-MS spectrum of

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$C_8H_5NO_2$ is characterized by CO_2 loss (Fig. S4j), indicative of a carboxyl group. Considering the degree of unsaturation of the $C_8H_5NO_2$ molecule and the cyano group feature in BB tracers (e.g., hydrogen cyanide, benzonitrile) (Schneider et al., 1997; Li et al., 2000; Gilman et al., 2015), $C_8H_5NO_2$ was identified as~~may be a~~ 4-cyanobenzoic acid using ~~,~~authentic standard (Fig. S5o). The $C_{10}H_{11}NO_4$, $C_{10}H_{11}NO_5$, $C_{11}H_{13}NO_5$, and $C_{11}H_{13}NO_6$ detected here are also observed in other BB experiments (Xie et al., 2019). Their MS-MS spectra are characterized by the loss of at least one CH_3 and/or OCN (Fig. S4r–u), suggestive of methoxy or cyanate groups. Without authentic standards, fragmentation patterns (Fig. S4r–u) were used to determine the molecular structures of $C_{10}H_{11}NO_4$, $C_{10}H_{11}NO_5$, $C_{11}H_{13}NO_5$, and $C_{11}H_{13}NO_6$ (Table S3).

Nearly all NAC formulas identified in this work were observed previously (Lin et al., 2016, 2017; Xie et al., 2017a; Fleming et al., 2018; Xie et al., 2019). Few studies attempt to retrieve structural information for NACs using MS-MS spectra of authentic standards. Although multiple NACs may be generated from BB and photooxidation of aromatics in the presence of NO_X, NAC structures may differ across emission sources. Xie et al. (2019) found that fragmentation patterns of $C_7H_7NO_5$ and $C_8H_9NO_5$ from BB and photochemical reactions are distinct, and the methoxy and cyanate groups are featured only in BB NACs. Thus, knowing the NAC structure is useful to emissions source identification. In this work, the chemical and structural information obtained for NACs sampled during red oak and charcoal burning are similar, presumably because the charcoal fuel used is produced by the slow pyrolysis of wood. However, NACs in red oak and charcoal burning emissions can be differentiated compositionally. As shown in Figs. 1 and S2, the NAC emissions from red oak burning in cookstoves are characterized by $C_{10}H_7NO_3$ and $C_{11}H_9NO_3$. In addition to these two species, charcoal burning in cookstoves also generates high fractions of $C_8H_9NO_5$ (Fig. S2c, d). This difference among NACs may help with source apportionment using

receptor models~~.~~, which are commonly used and assume that the ambient pollutants measured in the field are linear combinations from a number of time-variant sources/factors. (Jaeckels et al., 2007; Shrivastava et al., 2007; Xie et al., 2013).

Figure 2 compares NAC composition from cookstove emissions (not including $C_8H_5NO_2$), open BB (Xie et al., 2019), and SOA chamber experiments (Xie et al., 2017a). Since previous source emissions studies ignored Q_b measurements and normalized individual NACs concentrations to OM, only Q_f measurements in this work are compared (Fig. 2a, b) with their $iNAC_{OC}$% values multiplied by 1.7 (proposed OM/OC ratio, Reff et al., 2009). The three open BB tests (Fig. 2c) were conducted with two fuel types under different ambient temperatures (10–29 ^oC) and RH% (49–83%) (Xie et al., 2019). But they consistently emit $C_6H_5NO_4$, $C_7H_7NO_4$, and $C_9H_9NO_4$, which is compositionally distinct from cookstove emissions (Fig. 2a, b). Moreover, the average mass contribution of total NACs to OM for open BB (0.12 ± 0.051%) was 4–14 times lower than that for cookstove emissions. This result is likely due to the high temperature flaming combustion produced in the cookstoves (Shen et al., 2012; Xie et al., 2018). In Fig. 2d and e, the NAC profiles yielded for photochemical reactions appear to have aromatic precursors. When using field measurement data of NACs for receptor modeling, the resulting factors can be linked with specific emission sources by comparing with the NAC patterns shown in Fig. 2. Further studies are also warranted to unveil NAC patterns of other potential sources (e.g., motor vehicle emissions). Therefore, the source of NACs can be identified by combining their characteristic structures and composition. The filter-based NACs reported for the experiments shown in ~~Figure~~ Fig. 2 were all measured using the identical method and HPLC-Q-ToFMS instrument, reducing any potential methodological bias. However, total gas-phase NAC concentrations need to be properly sampled and measured to account for the impact of gas/particle partitioning on their distribution.

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3.4 Contributions of NACs to Abs_{365}

The average $Abs_{365,iNAC}$% values of Q_f and Q_b samples are presented by fuel type and WBT phase in the Fig. 3 stack plots, and experimental data for each fuel-cookstove are provided in Tables ~~S9~~S11–~~S12~~S14. The average contributions of total NACs to Abs_{365} ($Abs_{365,tNAC}$%) of the sample extracts (Q_f 1.10 – 2.~~58~~57%, Q_b 10.7 – 21.0%) are up to 10 times greater than their average $tNAC_{OC}$% (Q_f 0.31 – ~~0.97~~1.01%, Q_b 1.08 – 3.31%, Table 1). Considering that some NACs are not light-absorbing (Table S4) and the OM/OC ratio is typically greater than unity, most NACs that contribute to Abs_{365} are strong BrC chromophores. Like the mass composition of NACs (Fig. 1), $C_{10}H_7NO_3$ (CS 0.24%, HS 0.43%) and $C_8H_9NO_5$ (CS 1.22%, HS 0.55%) were the major contributors to Abs_{365} for the Q_f samples collected during red oak and charcoal burning, respectively (Fig.3a). The average $Abs_{365,tNAC}$% of Q_b samples are 7.53 to 11.3 times higher than those of Q_f samples. Unlike the Q_f samples from red oak burning, $C_{10}H_{11}NO_5$ (CS 2.77%, HS 3.09%) has the highest average contribution to Abs_{365} for Q_b samples, followed by $C_{10}H_7NO_3$ (CS 1.96%, HS 1.32%) and $C_8H_9NO_5$ (CS 1.32%, HS 1.44%). While $C_8H_9NO_5$ dominated the contribution (CS 8.78%, HS 5.82%) to Abs_{365} for the Q_b samples from charcoal burning (Fig. 3b). ~~However, the~~ All identified NACs ~~only~~ explained ~~a minor fraction (< 5%)~~ 1.10 – 2.58% (Fig. S3) of Q_f~~bulk~~ extracts absorption. Even if the NACs on Q_b were totally derived from upstream filter evaporation, the adjusted average contributions of total NACs (Q_f + Q_b) to Abs_{365} of Q_f extracts were still lower than 5% (1.59 – 4.01%). Due to the lack of authentic standards, the quantification of NACs concentrations and their contributions to Abs_{365} of Q_f extracts might be subject to uncertainties. However, growing evidences showed that BrC absorption was majorly contributed by large molecules with MW > 500 – 1000 Da (Di Lorenzo and Young, 2016; Di Lorenzo et al., 2017). Large molecules of NACs may be generated from flaming combustions in cookstoves, and

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their structures and light absorption are worth future investigations. ~~Chen and Bond (2010) hypothesized that BrC absorption is strongly associated with large molecules containing conjugated aromatic rings and functional groups. Additionally, Di Lorenzo et al. (2017) demonstrated that the majority of BrC absorption arises from large molecules with MW > 500–1000 Da.~~ In previous studies on ambient and biomass burning particles, most identified NACs had a MW lower than 300 – 500 Da, and their total contributions to bulk BrC absorption were estimated to be less than 10% (Mohr et al., 2013; Zhang et al., 2013; Teich et al., 2017; Xie et al., 2019). Similar results were also obtained in the current work. Therefore, further studies are needed to identify large BrC molecules (including high MW NACs) in ambient and source particles. ~~In previous studies, less than 10% of the BrC absorption at λ = 365 nm from ambient or BB particles are ascribed to NACs with MW < 300 Da. Further studies are needed to identify these larger molecules that are the dominant light absorbers in BB and cookstove PM. The average $Abs_{365,tNAC}$% of Q_b samples are 7.52 to 11.3 times higher than those of Q_f samples. Unlike the Q_f samples from red oak burning, $C_{10}H_{11}NO_5$ (CS 2.77%, HS 3.09%) has the highest average contribution to Abs_{365} for Q_b samples, followed by $C_{10}H_7NO_3$ (CS 1.96%, HS 1.32%) and $C_8H_9NO_5$ (CS 1.32%, HS 1.44%). While $C_8H_9NO_5$ dominated the contribution (CS 8.78%, HS 5.82%) to Abs_{365} for the Q_b samples from charcoal burning (Fig. 3b). As mentioned in section 3.2, some NACs identified in this work might have substantial gas-phase concentrations. Jacobson (1999) inferred that the nitrate-bearing aromatic gases may play a role in reducing the UV irradiance within the boundary layer in Los Angles during 1973 – 1987. Therefore, we suspect that gaseous NACs may be an important group of molecules absorbing in short UV region in the atmosphere.~~

4 Conclusion

This study investigated the composition, chemical formulas, and structures of NACs in $PM_{2.5}$ emitted from burning red oak and charcoal in a variety of cookstoves. Total NAC mass and compositional differences between Q_f and Q_b samples suggest that the identified NACs might have substantial gas-phase concentrations. By comparing the MS-MS spectra of identified NACs to standard compound spectra, the structures of NACs featuring methoxy and cyanate groups in cookstove emissions are confirmed. The source identification of NACs would be less ambiguous if both the structures and composition of NACs are known, as different emission sources have distinct NAC characteristics. However, the compositional information of NACs based on Q_f measurements only are biased due to the lack of gas-phase data, and further studies are warranted to investigate the gas/particle distribution of NACs in the ambient and source emissions. Similar to previous work, the average contribution of total NACs to Abs_{365} of Q_f samples is less than 5% (1.10 – 2.~~58~~57%), suggesting the need to shift our focus from low MW NACs (MW < 300 Da) to the chemical and optical properties of large molecules (e.g., MW > 500 Da) in particles. ~~However, their average contributions to Abs_{365} of Q_b samples are 7.52 to 11.3 times higher, so NACs may be important light absorbers in the gas phase. Further research in understanding the influence of gaseous chromophores on the earth's radiative balance is warranted.~~

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Data availability

Data used in the writing of this manuscript is available at the U.S. Environmental Protection Agency's Environmental Dataset Gateway (https://edg.epa.gov).

Competing interests

The authors declare that they have no conflict of interest.

Disclaimer

The views expressed in this article are those of the authors and do not necessarily represent the views or policies of the U.S. Environmental Protection Agency.

Author contribution

MX and AH designed the research. MX, ZZ, and XC performed the experiments. GS, WC, and JJ managed cookstove emission tests and sample collection. MX and MH analyzed the data and wrote the paper with significant contributions from AH and QW.

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Table 1. Average concentrations of total NACs and $tNAC_{OC}$% in Q_f and Q_b samples by fuel type and WBT phase.

Fuel &Test phase	Red Oak		Charcoal	
	CS	HS[a]	CS	HS
		Front filter (Q_f)		
Sample number	18	17[b]	15	15
total NAC (μg m^{-3})	3.43 ± 1.37	3.91 ± 2.06	0.51 ± 0.43	1.00 ± 0.48
$tNAC_{OC}$%	1.01 ± 1.06	0.98 ± 1.09	0.40 ± 0.25	0.31 ± 0.21
OC (μg m^{-3})[c]	624 ± 410	908 ± 885	115 ± 72.0	447 ± 271
EC/OC[c]	1.74 ± 1.42	1.96 ± 1.74	6.12 ± 2.76	0.029 ± 0.012
		Backup filter (Q_b)		
Sample number	18	17[b]	14[b]	15
total NAC (μg m^{-3})	1.67 ± 0.76	1.79 ± 0.77	0.37 ± 0.31	1.30 ± 0.70
$tNAC_{OC}$%	3.31 ± 3.46	2.77 ± 2.66	1.10 ± 0.89	1.08 ± 0.51
OC (μg m^{-3})[c]	78.4 ± 43.2	100 ± 58.4	41.9 ± 23.3	138 ± 70.8
		Q_b/Q_f ratio (%)		
total NACs	50.8 ± 13.4	53.4 ± 26.2	84.1 ± 38.0	140 ± 52.9
OC[c]	14.8 ± 3.87	15.3 ± 6.37	35.4 ± 12.2	38.8 ± 18.9

[a] Including three SIM phase samples from the 3-stone fire; [b] one filter sample was missed for analysis; [c] data were obtained from Xie et al. (2018).

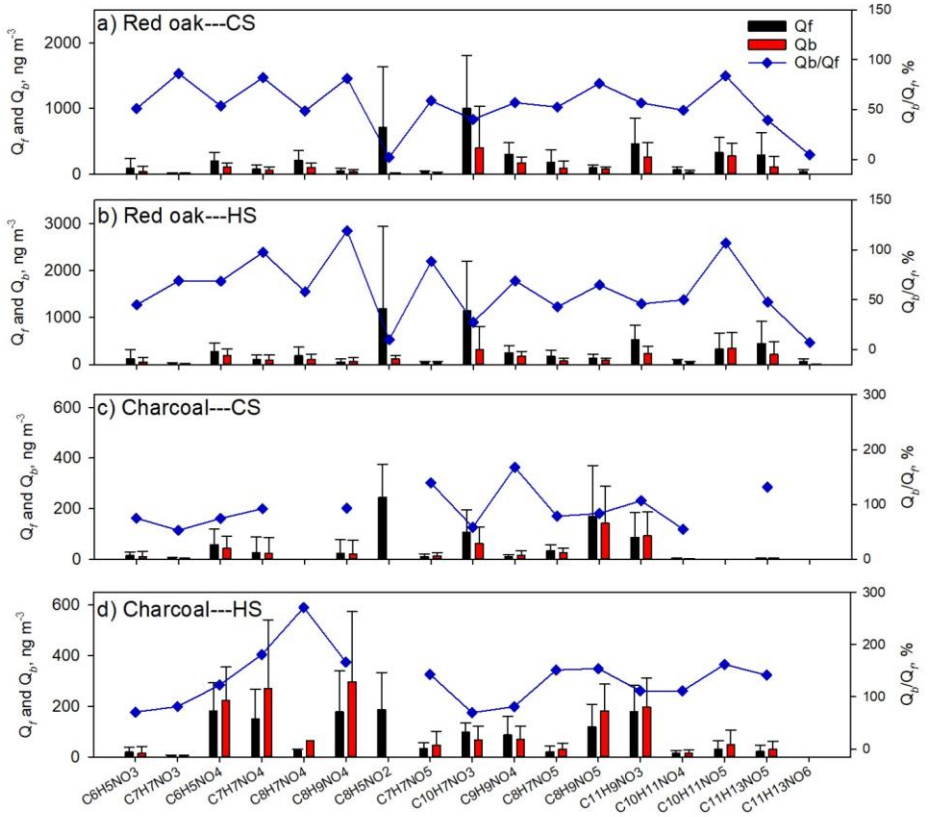

Figure 1. Average concentrations of individual NACs in Q_f and Q_b samples for (a) red oak burning under the CS phase, (b) red oak burning under the HS phase, (c) charcoal burning under the CS phase, and (d) charcoal burning under the HS phase. The blue scatters in each plot are mass ratios of individual NACs in Q_b to Q_f samples × 100%.

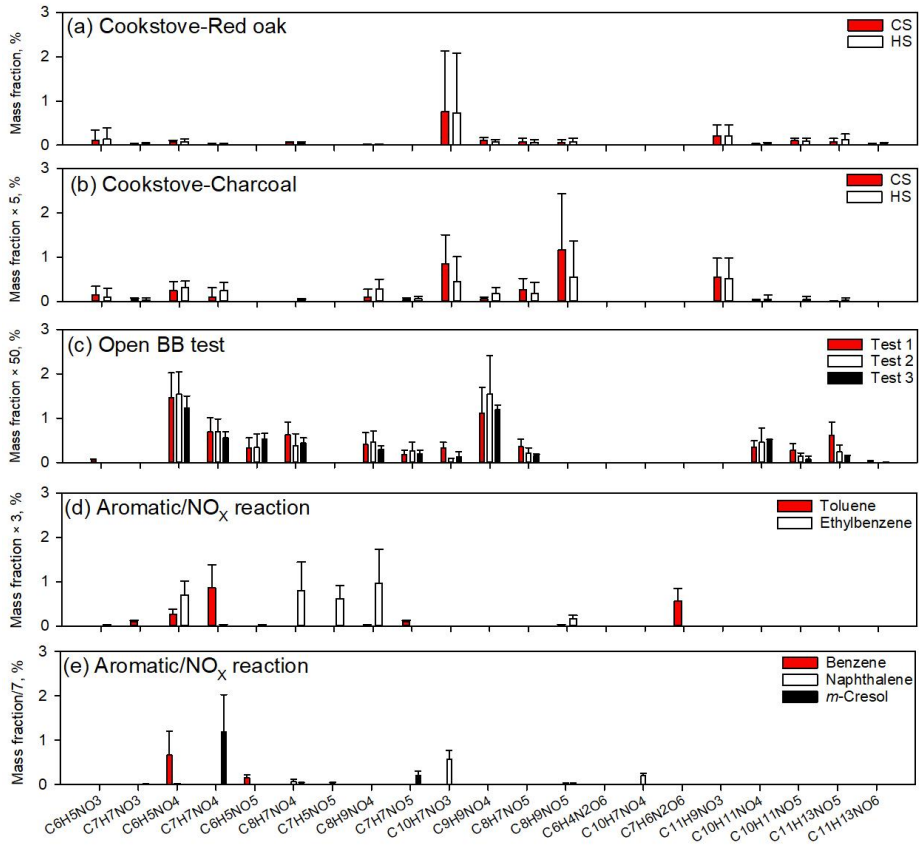

Figure 2. Average mass ratios (%) of individual NACs to organic matter from (a) red oak burning in cookstoves, (b) charcoal burning in cookstoves, (c) open BB experiments (Xie et al., 2019), photochemical reactions of (d) toluene and ehthylbenzene, and (e) benzene, naphthalene, and m-cresol with NO_X (Xie et al., 2017a).

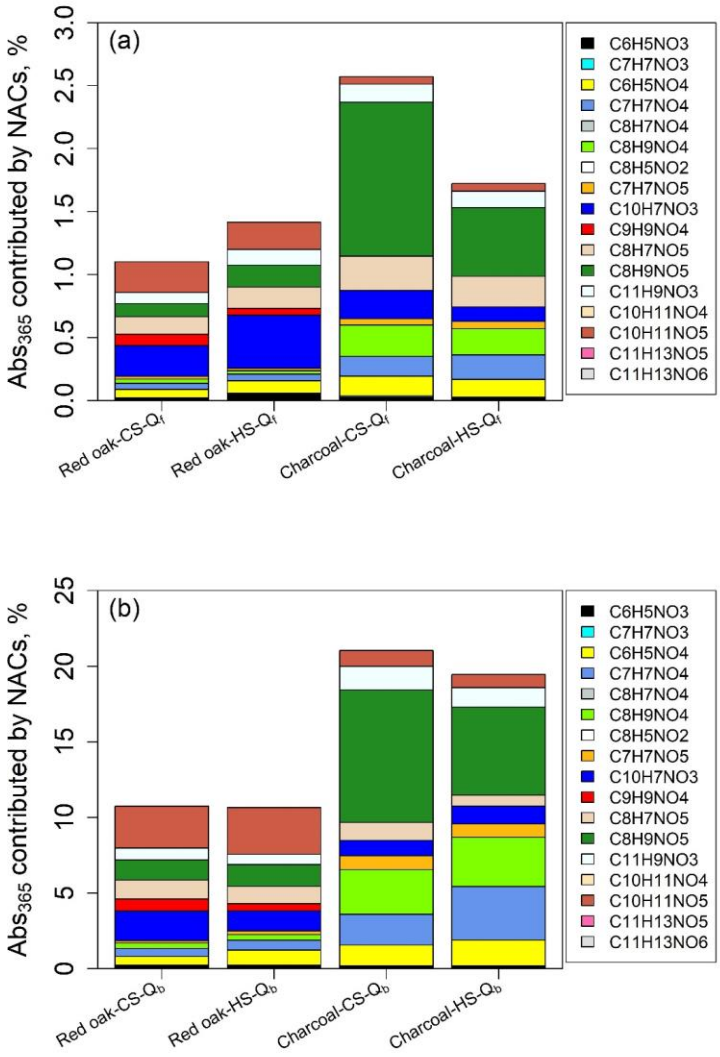

Figure 3. Average contributions (%) of individual NACs to bulk extracts Abs_{365} of (a) Q_f, and (b) Q_b samples from burning red oak and charcoal in cookstoves under CS and HS phases.