

Responses to the Reviewer's Comment

We thank the reviewer for the constructive and insightful comment. Our point-by-point responses can be found below, with reviewer comments in **black**, our responses in **blue**, alongside the relevant revisions to the manuscript in **red**.

RC#1

General comments:

This study constructs a near-complete chemical description of ROG emissions from residential coal and biomass combustion using GC-MS/FID and Vocus PTR-ToF-MS. ROG emissions were underestimated by $44.3 \pm 11.8\%$ and $22.7 \pm 3.9\%$, considering the un-characterized species, which resulted in the underestimation of SOA formation potential and OH reactivity. In the current framework, 125 species were quantified, accounting for approximate 90% of the total ROG emission. SOAP and OHR were re-estimated incorporating the newly identified species and the spatial distribution and annual variation of ROG emissions from residential coal and straw combustion in China are reported. The topic is covered by ACP and the data is of interests to relevant readers. However, novelty is lacking with respect to methodology and results and the discussion lacks depth. Also, the manuscript is not well drafted, mistakes and errors are commonly seen.

R:

ROG emissions from residential combustion especially biomass combustion have been widely studied due to their great contribution to global ROG emissions and the complexity of compositions. Among them, studies focusing on the ROG speciation for residential combustion could generally be divided into three categories according to the measurement methods, as listed in Table R1. The first one was the whole-air sampling with offline analysis by one-dimensional gas chromatography system equipped with a mass spectrometer and/or a flame ionization detector (GC-MS/FID), which mainly focused on the hydrocarbons ($<C_{12}$) (Mo et al., 2016; Wang et al., 2013; Liu et al., 2008). With the development of the advanced instruments, the second category of studies on ROG emissions gave more attention to the polar species like oxygenated ROG emissions, which could be online detected through the whole combustion process mainly by proton transfer reaction time-of-flight mass spectrometry (H_3O^+ PTR-ToF-MS) due to the high mass resolution and sensitivity (Cai et al., 2019; Bruns et al., 2017; Stockwell et al., 2015; Koss et al., 2018; Akherati et al., 2020; Wu et al., 2022). Considerable (approximately 6%-24%) species with intermediate volatility in residential ROG emissions were identified as the large contributors of secondary organic aerosols (SOA) (Cai et al., 2019; Koss et al., 2018).

Thirdly, due to the inability to isolate isomers by H_3O^+ PTR-ToF-MS and considerable amount of oxygenated ROG emissions with intermediate volatility in residential ROG emissions, the increasing interest has been put on the application and comparisons of multiple instruments for the detailed identification of ROG species (Koss et al., 2018; Hatch et al., 2017). More than 150 PTR ion masses

were identified using the combination of techniques including GC pre-separation, two-dimensional GC system (GC×GC), fourier transform infrared spectroscopy (FTIR), and NO⁺ chemical ionization mass spectrometer (NO⁺ CIMS), which contributed ~90% of the ROG masses detected by H₃O⁺ PTR-ToF-MS in biomass combustion emissions (Koss et al., 2018). The comparisons demonstrated that H₃O⁺ PTR-ToF-MS might be the most suitable for the detection of the lowest-volatility and most polar species, which covered the most (50%-79%) species, comparing with the other instruments, in the combined ROG measurement covering more than 500 species from different instruments (Koss et al., 2018; Hatch et al., 2017).

Recently, the higher alkanes (≥C₈), one kind of considerable species in residential combustion emissions (Jathar et al., 2014; Huo et al., 2021; Li et al., 2023), which were not included in the comprehensive measurements of previous studies (Hatch et al., 2017), could be well measured by PTR-ToF-MS with NO⁺ ion chemistry (Wang et al., 2020a; Koss et al., 2016). Thus, PTR-ToF-MS might be a preferent and promising method for the development of near-complete ROG speciation relevant for residential combustion, but need to combine with GC-MS/FID for the complement measurement of aliphatic hydrocarbons. Compared to the comprehensive measurements by more instruments previously, the combination of PTR-ToF-MS and the GC-MS/FID method was labor-saving and further could minimize the measurement uncertainties from the synthesis of measurement data due to fewer kinds of instruments. Therefore, the present study focused on (1) developing the near-complete ROG speciation through quantifying all signals by H₃O⁺ PTR-ToF-MS and supplementing C₂-C₂₂ aliphatic hydrocarbons by GC-MS/FID and NO⁺ PTR-ToF-MS, and (2) the composition of ROG emissions through the real combustion sampling in rural household of China. Finally, the near-complete ROG speciation further supported the estimation of the ROG emissions from residential combustion in China as well as their hydroxy radical reactivity and formation potential of SOA. The present study took the residential combustion as an example for developing the near-complete ROG speciation mainly considering the large complexity of combustion-relevant ROG speciation and the comprehensive measurement of residential combustion previously, which could be used to further confirm the present result by overlapping species.

We have revised it in the sections of Abstract and Introduction in the revised manuscript.

Table R1 Review on the measurements of ROG emissions from the residential combustion.

Method	Fuel types	Reference	Numbers of species		
			GC-MS/ FID	PTR-ToF-MS	Other instruments
Combustion in stove	Residential coals, biomass (straw and wood) from China	This study	71	84 (84-92% of the overall peak mass)	—
	Corn cob from China	(Wu et al., 2022)	—	13	—
	Anthracite, bituminous coal from China	(Cai et al., 2019)	—	79-89 (90-96% of the overall peak intensities)	—
	Beech (<i>Fagus sylvatica</i>) logs	(Bruns et al., 2017)	—	64 (94-97% of the total mass)	—
	Biomass (peanut shell, maize straw), raw	(Wang et al., 2013)	60	—	24 (DNPH- HPLC ^a)

Method	Fuel types	Reference	Numbers of species		
			GC-MS/ FID	PTR-ToF-MS	Other instruments
Combustion simulation in Lab	coals from China				
	Biomass fuels from the western US	(Akherati et al., 2020)	—	150	—
	Burned fuels from the western US	(Koss et al., 2018)	—	172 (~95% of the overall peak intensities)	15 (FTIR ^b), 261 (GC-CIMS ^c)
	Four burns: ponderosa pine boughs, Chinese rice straw, Indonesian peat, and black spruce boughs	(Hatch et al., 2017)	~27	~71	~13 (FTIR) ~418 (GC×GC)
	Authentic globally significant fuels	(Stockwell et al., 2015)	—	46-92	—
	Biomass burns of 18 fuel types from 3 geographic regions in the US	(Gilman et al., 2015)	187	Unpublished	Unpublished (FTIR)
	Residential coal, rice, maize, and wheat straw from China	(Mo et al., 2016)	62	—	13 (DNPH-HPLC)
	biomass, residential coal from China	(Liu et al., 2008)	92	—	—

Note:

^a, DNPH-HPLC: 2, 4-Dinitrophenyl hydrazine followed by high performance liquid chromatography (HPLC).

^b, FTIR: Fourier transform infrared spectroscopy.

^c, GC-CIMS: Gas chromatography chemical ionization mass spectrometry.

Specific comments:

Q1: Line 113-116. PTR-MS with H₃O⁺ detects the VOC molecules with higher proton affinity than water and PTR-MS with NO⁺ extends the range of compounds that can be detected. As you mentioned, a total of 1005 peaks were extracted with m/z lower than 200 in H₃O⁺ mode and selected peaks in NO⁺ mode.

(1) What are the range of compounds that NO⁺ mode supplements and the criteria of selecting these compound species?

R:

NO⁺ PTR-ToF-MS in this study is only used for a supplementary measurement of higher alkanes (≥C₈). The criteria of selecting these species were that (1) the species could not be measured well by H₃O⁺ PTR-ToF-MS, (2) the methods of which have been well-established by NO⁺ PTR-ToF-MS previously. More details are as follows.

Multi-instruments were deployed to measure ROG_s in the emissions of residential combustion,

aiming to develop a near-complete speciation of ROGs in this study, which included H_3O^+ PTR-ToF-MS, NO^+ PTR-ToF-MS, and GC-MS/FID. H_3O^+ PTR-ToF-MS could identify the ROGs as long as the proton affinity of ROGs greater than that of water (691 kJ mol^{-1}) (Yuan et al., 2017), with relatively complete species coverage. It may be the preferred method toward ROGs complete measurement, because most ROGs can be detected (Li et al., 2020; Krechmer et al., 2018) and the sensitivity for a given ROG can be calculated theoretically (Sekimoto et al., 2017) by H_3O^+ PTR-ToF-MS.

Despite these advantages, H_3O^+ PTR-ToF-MS has two limitations related to the reagent ion chemistry. Firstly, the technique is insensitive to C2-C7 alkanes, ethene and acetylene with lower proton affinity than water (Jobson et al., 2009). Here, these common constituents of urban atmospheres were well-measured by traditional technology such as GC-MS/FID. Secondly, higher alkanes ($\geq \text{C}_8$), one kinds of important components of the fuel combustion (Huo et al., 2021; Jathar et al., 2014), were difficult to quantify by H_3O^+ PTR-ToF-MS due to fragments produced during the ionization process. NO^+ PTR-ToF-MS has been demonstrated to provide a supplementary measurement of higher alkanes (Wang et al., 2020a; Koss et al., 2016).

Different from H_3O^+ PTR-ToF-MS by which the sensitivity for a given ROG can be calculated theoretically even without the standard for calibration, authentic standards are necessary for quantification by NO^+ PTR-ToF-MS, which limited the characterization of mass spectrum ionized by NO^+ . The difficulty to predict the ionized ROG products and to interpret the mass spectrum unambiguously further limited its application in ROG speciation, because NO^+ has three common reaction mechanisms with ROGs: charge transfer, hydride abstraction, and cluster formation (Koss et al., 2016). Therefore, NO^+ PTR-ToF-MS in this study was only used for a supplementary measurement of higher alkanes ($\geq \text{C}_8$) with a well-established quantitative method (Wang et al., 2020a).

(2) What are the organic gases that are not sensitively detected by PTR-MS with H_3O^+ and NO^+ modes and how can GC/MS-FID complement the measurement? This information should be included, either in the main text or the SI. Currently, the analysis section is brief.

R:

The two limitations of PTR-ToF-MS with H_3O^+ on organic gas detection are given in the reply to the previous question Q1(1). Briefly, the technique is limited in the detection of aliphatic hydrocarbons involving alkanes, alkenes and alkynes. NO^+ PTR-ToF-MS has been demonstrated to provide a supplementary measurement of higher alkanes ($\geq \text{C}_8$) (Wang et al., 2020a; Koss et al., 2016). With NO^+ PTR-ToF-MS, light alkanes and unsaturated aliphatic hydrocarbons were not yet well measured, which were subject to the interference from fragments producing by many different species. The GC-MS/FID could provide a supplementary measurement of these species against PTR limitations. Besides, GC/MS-FID provided isomer speciation which is incapable for PTR-ToF-MS with both H_3O^+ and NO^+ .

We have clarified it more clearly in Section 2.2 and Section 2.3 of the revised manuscript as following:

Section 2.2.4, the first paragraph:

“H₃O⁺ PTR-ToF-MS could identify the ROGs as long as the proton affinity of ROGs greater than that of water (691 kJ mol⁻¹) (Yuan et al., 2017), with relatively complete species coverage. It may be the preferred method toward ROG complete measurement, because most ROGs can be detected (Li et al., 2020; Krechmer et al., 2018) and the sensitivity for a given ROG can be calculated theoretically by H₃O⁺ PTR-ToF-MS (Sekimoto et al., 2017). Despite these advantages, H₃O⁺ PTR-ToF-MS has two limitations related to the reagent ion chemistry. Firstly, the technique is insensitive to C2-C7 alkanes, ethene and acetylene with lower proton affinity than water (Jobson et al., 2009). Secondly, higher alkanes (≥C8), one kinds of important components of the fuel combustion (Huo et al., 2021; Jathar et al., 2014), were difficult to quantify by H₃O⁺ PTR-ToF-MS due to fragments produced during the ionization process.”

Section 2.3.1, the first paragraph:

“NO⁺ PTR-ToF-MS has been demonstrated to provide a supplementary measurement of higher alkanes (Wang et al., 2020a; Koss et al., 2016). Different from H₃O⁺ PTR-ToF-MS by which the sensitivity for a given ROG can be calculated theoretically even without the standard for calibration, authentic standards are necessary for quantification by NO⁺ PTR-ToF-MS, which limited the characterization of mass spectrum ionized by NO⁺. The difficulty to predict the ionized ROG products and to interpret the mass spectrum unambiguously further limited its application in ROG speciation, because NO⁺ has three common reaction mechanisms with ROGs: charge transfer, hydride abstraction, and cluster formation (Koss et al., 2016). Therefore, NO⁺ PTR-ToF-MS in this study was only used for a supplementary measurement of higher alkanes (≥C8) with a well-established quantitative method (Wang et al., 2020a).”

Section 2.3.2, line 215-217:

“Against PTR limitations (Arnold et al., 1998; Gueneron et al., 2015), GC-MS/FID with a cryogen-free preconcentration device was also deployed.”

Q2: Figure 1, when conducting the mass closure analysis, how to quantify the organic gases that are not effectively detected by PTR-MS and GC-FID/MS. Given FID is adopted, THC data (if any) may help.

R:

In this study, we assumed the “total” ROGs including all signals quantified by H₃O⁺ PTR-ToF-MS and supplementing C2-C22 aliphatic hydrocarbons measured by GC-MS/FID and NO⁺ PTR-ToF-MS, mainly due to the broad species coverage of PTR. Koss et al. (2018) made an intensive comparison of different instruments for ROG measurements of emissions of biomass combustion, including GC pre-separation, two-dimensional GC system (GC×GC), fourier transform infrared spectroscopy (FTIR), NO⁺ chemical ionization mass spectrometer (NO⁺ CIMS) and H₃O⁺ PTR-ToF-MS. The comparison demonstrated that H₃O⁺ PTR-ToF-MS might be the most suitable for the detection of the lowest-volatility and most polar species, which covered the most (50%-79%) species, comparing with the other instruments, in the combined ROG measurement covering more than 500 species from different instruments (Koss et al., 2018). Thus, H₃O⁺ PTR-ToF-MS might be a preferent and promising method for the development of near-complete ROG speciation relevant

for residential combustion, but need to combine the measurement of aliphatic hydrocarbons. Here, the C₂-C₂₂ aliphatic hydrocarbons, not well measured by H₃O⁺ PTR-ToF-MS, have been supplemented by GC-MS/FID and NO⁺ PTR-ToF-MS. From the technological point of view, the ROG_s by simplified instrument deployment in this study might represent the total ROG_s to some extent based on all current state-of-the-art technologies.

As the reviewer suggested, the total hydrocarbons (THCs) provide a potential path towards mass closure (carbon budget). The feasibility for mass closure analysis using the THCs data has been discussed in terms of the instrument measurement fundamentals and the experimental results as below.

(1) Measurement fundamentals

The concentration of total hydrocarbon in gas samples is generally detected by the flame ionization detector (FID). According to the FID ionization mechanism, the main reason of signal detection by FID is that the carbon atoms of organic compounds produce CHO⁺ in the hydrogen flame. Thus, the number of carbon atoms in organic compounds per unit mass determine the FID response value of organic compounds (Sun, 1979). However, the types of organic compounds affect the efficiency of CHO⁺ formation. For most hydrocarbons, such as normal and isomeric alkanes, alkenes etc., the response signal per gram of carbon should be relatively consistent. While, FID detector has a more variable and smaller response to oxygenated organic compounds than hydrocarbons. Only some carbon could form positive ions when carbon and oxygen are connected by single bond, and it is almost impossible for carbon to form positive ions when double bonds occur between carbon and oxygen (Fan et al., 2002).

The photoionization detector (PID) is an alternative technology for THCs measurement. Similar to the FID, the PID also converts the organic compounds into an ion stream for detection, while the energy of ionization is provided by an ultraviolet lamp instead of a hydrogen flame. The PID techniques also suffers from low and variable response towards oxygenated organic compounds (Yang and Fleming, 2019; Cai et al., 2019).

(2) Experimental results

Cai et al. (2019) has made an attempt on comparison between the THCs (except methane) detected by a portable analyzer (JiShunAn JK40, Shenzhen, China) equipped with a PID module (noted as PID) and the sum of organic species (ΣROG) detected by the PTR-ToF-MS. THC emissions by PID were always lower than ΣROG emissions of the PTR-ToF-MS throughout the combustion cycle (Cai et al., 2019). Thus, it is expected that the ROG emissions detected by PTR-ToF-MS and GC-MS/FID in current work exceed THC emissions and mass closure analysis using THCs is not appropriate.

Therefore, this work overlooked the organic gases not effectively detected by PTR-MS and GC-MS/FID and highlighted the detailed chemical understanding based on all current state-of-the-art technologies. The total ROG_s requires further advances in directly analytical measurements.

Q3: Line 118, 162 ions with a relative high degree of certainty... Again, the introduction of the data treatment is inadequate. What is the standard of selecting these ions and how to determine the

certainty threshold. Similar question goes to line 156, 87 out of 162 species were used....please give more details regarding data treatment.

R:

In order to clearly introduce the data treatment of deployed instruments in this study, H_3O^+ PTR-ToF-MS is introduced separately from NO^+ PTR-ToF-MS and GC-MS/FID measurement and the Section 2 Analysis in the main text is reorganized as below.

(1) Analysis by H_3O^+ PTR-TOF

H_3O^+ PTR-ToF-MS served as the primary equipment toward ROG complete speciation due to the detectability of most ROGs with relatively complete species coverage (Li et al., 2020; Krechmer et al., 2018) and theoretically computable sensitivity (Sekimoto et al., 2017). All valid signals in raw mass spectrum were (i) identified, (ii) quantified, and (iii) analyzed for uncertainty, following the detailed process of data treatment shown in Fig. R1.

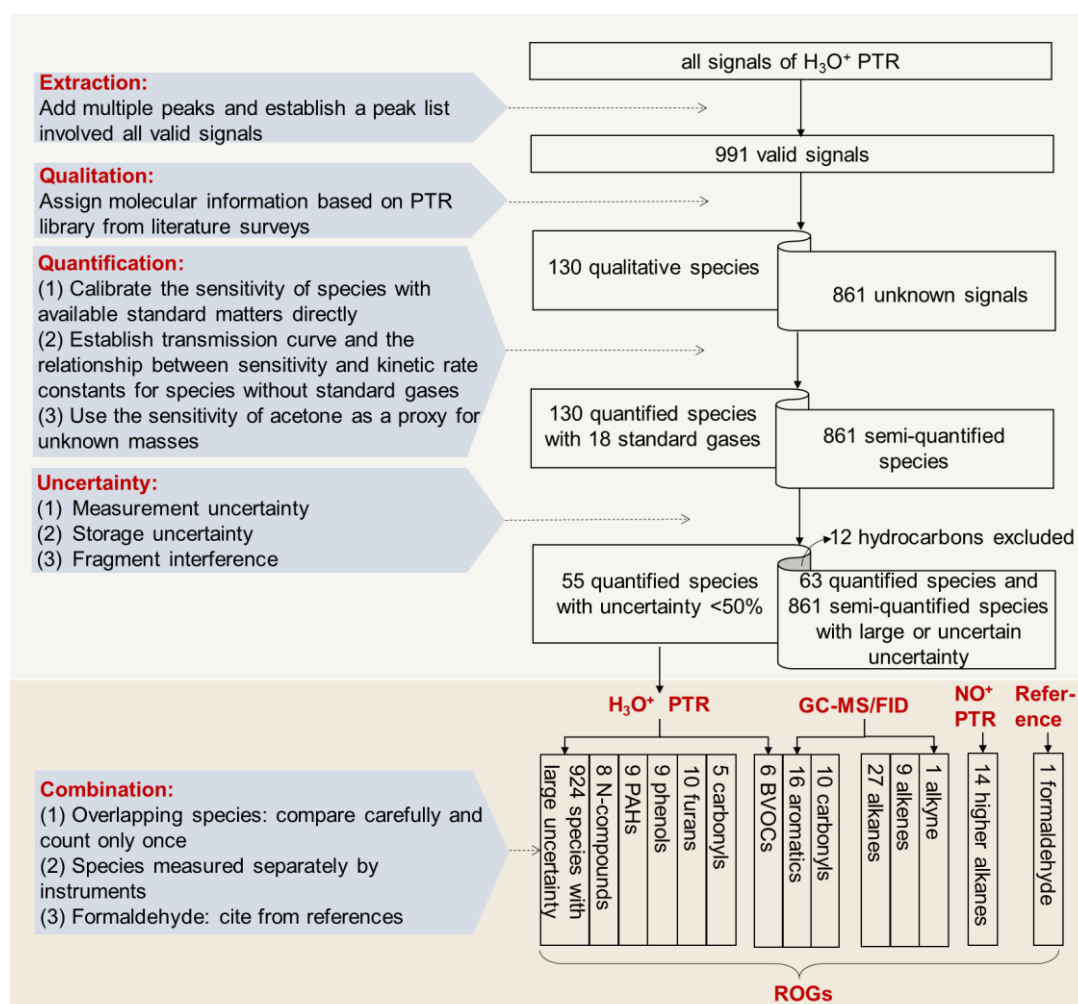


Figure R1. Diagram of data treatment to obtain the near-complete ROG speciation.

(i) Identification

A total of 991 valid ion masses were extracted from original mass spectrum through multi-peak

fitting (Stark et al., 2015), of which 130 species were well-qualitative while 861 signals were still unknown according to literature surveys (Pagonis et al., 2019; Koss et al., 2018; Stockwell et al., 2015).

Extraction (991 masses). The raw mass spectrum data of gaseous ROGs measured by H_3O^+ PTR-ToF-MS were mainly distributed in the range of m/z 40- m/z 200 (Koss et al., 2017), with a mass resolution of $10000\text{ m}\Delta\text{m}^{-1}$. Multiple peaks were added at each nominal mass below m/z 200 resulting in a peak list of 991 valid masses in the software Tofware package v3.2.3 (Tofwerk Inc.).

Qualitation (130 specific ROGs and 861 unknown masses). Based on accurate m/z , isotope pattern and published PTR library from the review of 49 publications (containing 226 molecules and nearly 1000 species) (Pagonis et al., 2019) and local PTR library (Yuan et al., 2022; Gao et al., 2022), molecular information of individual mass was calculated and matched. Due to the complexity of isomers, the recommended names of various species were further determined by the combustion-relevant reports of Koss et al. (2018) and Stockwell et al. (2015) (Koss et al., 2018; Stockwell et al., 2015). Finally, 130 masses matched with proposed species, while the remaining 861 peaks were defined as unknown masses with molecular formulas but without recommend species or only with accurate m/z without elemental composition calculated.

(ii) Quantification

Sensitivities of all the masses in this work were obtained by (1) calibration by authentic standard for species with standard matters available, (2) theoretical calculation by the relationship between sensitivity and kinetic rate constants (k) (Sekimoto et al., 2017) for identified species without commercial standards, or (3) estimation using the sensitivity of acetone as a proxy for unknown masses.

Calibration method (18 species). The sensitivities of 18 species were calibrated experimentally by introducing multi-gradient known concentrations of given ROGs from a customized cylinder (Linde Gas North America LLC, USA). These standard gases included benzene, toluene, styrene, m-xylene, 1,3,5-trimethylbenzene, m-diethylbenzene, isoprene, α -pinene, acetaldehyde, acrolein, acetone, methyl vinyl ketone, methyl ethyl ketone, 2-pentanone, methyl isobutyl ketone, acetonitrile, furan, and naphthalene. More details of the calibration could be found in our previous studies (Gao et al., 2022; Wang et al., 2020b).

Calculation method (112 species). For other well qualitative species without available standards, we used the method proposed by Sekimoto et al. (2017) to theoretically calculate the concentrations by the relationship between ROG sensitivities and kinetic rate constants (k_{kinetic}) for proton transfer reactions of H_3O^+ with ROGs (Fig. S2 in the Supplementary Information), which was established by the calibrated species above.

Estimation method (861 masses). For unknown masses, it is difficult to estimate k_{kinetic} which depends on molecular properties, and the sensitivity of acetone was used as a proxy (Cai et al., 2019).

(iii) Uncertainty analysis

The measurement uncertainty of a specific ROG is mainly from the analysis and storage. The analysis uncertainty depending on the quantification method in Section 2.2.2 was estimated

following the method of Sekimoto et al. (2017). The effect of storage inside the canister was evaluated using the standard samples with different storage duration in the laboratory. Accordingly, the total measurement uncertainties of different ROG species were estimated, as listed in Table S2 in the Supplementary Information.

Analysis uncertainty. The analysis uncertainty corresponds to the three kinds of quantification methods. Firstly, the experimentally calibrated species have an upper-bound analysis uncertainty of 15%, including those of analysis precision and calibration factors (Gao et al., 2022), as shown in Table S2 in the Supplementary Information. Secondly, for those species quantified by theoretical calculation, the uncertainty was mainly attributed to the estimated value of k_{kinetic} and the linear regression slope ($\sim 20\%$ from fitting bias in this study) between sensitivity and k_{kinetic} , which was within 50% (Sekimoto et al., 2017). Thirdly, for unknown masses, the uncertainty was mainly from the difference of their “real” sensitivities from the assumed sensitivity of acetone, which was dependent on the difference of their k_{kinetic} . Generally, the oxygenated species ($\text{C}_x\text{H}_y\text{O}_z$) have higher ($\sim 2.5\text{--}3.5 \times 10^{-9} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) k_{kinetic} than those of aliphatic hydrocarbons (C_xH_y , $\sim 2 \times 10^{-9} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$), and the k_{kinetic} of acetone is $3.23 \times 10^{-9} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (Cappellin et al., 2012). Thus, the maximum uncertainty of the estimated concentrations of unknown masses caused by this assumption is estimated to be 65% although the “real” k_{kinetic} is as low as $2 \times 10^{-9} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ in this study.

Loss in storage. To evaluate the possible artifacts caused by the SUMMA canister storage, the sensitive tests of the storage duration were carried out by the standard samples in laboratory. Standard samples including 85 species, with a known concentration (5 ppbv in this study) were prepared into clean vacuum SUMMA canisters and detected within 2h as well as on days 1, 2, 4, 7, 10 and 14 after preparation. Here, the loss fraction was estimated to be the maximum threshold because the mixing ratios of most observed ROGs in all samples were normally higher than 5 ppbv. The detailed species and deviations were shown in Fig. S3 (in the Supplementary Information). The storage loss on day 10th was used considering that samples were analyzed within 9 days after sampling in this work (Table S2 in the Supplementary Information). According to experimental results, the loss of some carbonyls (-CHO and RCO-), furans and nitrogenous species (-CN) was measured within 20%, while the loss of several alcohols (-OH) exceeded 50%. The results of carbonyls were comparable with previous studies in which the half-lives of aldehydes were 18 days in the canister (Batterman et al., 1998). The higher polarity of alcohols is a possible reason for their larger loss proportion, as the polar species preferentially adsorbed on surface sorption sites of SUMMA canister inner walls (Batterman et al., 1998). Although volatility is another potential factor, in current experimental results for 10 days, the loss proportion has no significant dependence on volatility (Fig. R2).

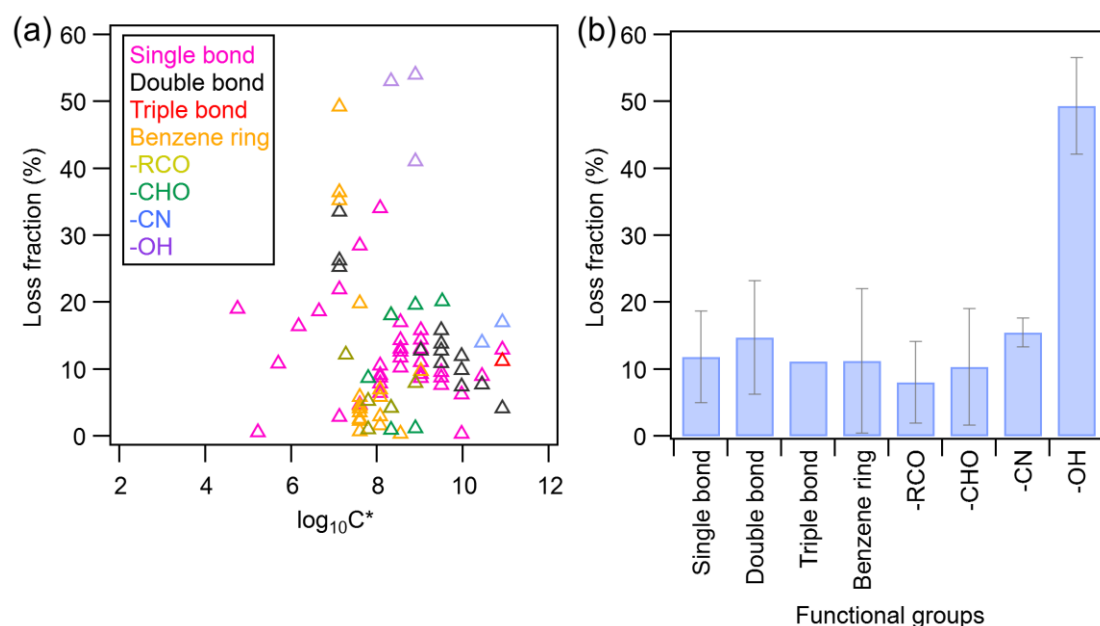


Figure R2. Plots of the loss fraction versus volatility (the logarithmic effective saturation vapor concentration, $\log_{10}C^*$) and polarity (functional groups) of species respectively. (a) The scatter plot of the loss fractions of individual species and $\log_{10}C^*$, colored by functional groups (see legend). (b) The average and standard deviation of loss fraction for species with the same functional groups.

For the other species of carbonyls, furans and nitrogenous species without standards, their loss during storage was assumed as the measured largest loss fraction in the same category. For phenols, an important category in ROG emissions from residential combustion (Bruns et al., 2016), their loss was believed to be predictable considering that phenols have been mentioned suitable for canister sampling in US EPA method TO15 (Epa/625/R-96/010b, 1999) and was estimated as 20% referring to the largest loss fraction of measured carbonyls. For other categories such as acids (-COOH), species with more than 2 oxygen atoms (usually 2 functional groups) and components containing -NO_n, there were no standards used to evaluate the loss during storage. Overall, 63 specific ROGs with large uncertainty potentially (>50%) and 861 unknown masses with uncertain loss fraction were only used to quantify the total ROGs and were excluded from the further discussion of ROG composition.

Fragment interference. The aliphatic hydrocarbons such as C₃H₆H⁺, C₄H₈H⁺ are interfered by fragments from different species. In this work, 12 such ions were excluded from the results to avoid the uncertainty, due to well-characterized hydrocarbons were provided by GC-MS/FID.

In summary, except for 12 aliphatic hydrocarbon fragments, the other 979 detected masses by H₃O⁺ PTR-ToF-MS were used in this study, among which 55 species with the uncertainty ranging from 1% to 44% were used in further discussion of ROG composition, and the rest masses with larger (>50%) or unknown uncertainty potentially were only used to quantify the total ROGs in Fig. R3.

(2) Species combination

Aiming to develop a near-complete speciation of ROGs in this study, NO⁺ PTR-ToF-MS, and GC-MS/FID were deployed additionally against the limitations of H₃O⁺ PTR-ToF-MS discussed above,

which was highly complementary, with covering some unique and important range of compositional space. During the species combination for a near-complete speciation of ROGs, overlapping measurements of the same species should be counted only once.

(i) NO⁺ PTR-ToF-MS

NO⁺ PTR-ToF-MS has been demonstrated to provide a supplementary measurement of higher alkanes (Wang et al., 2020a; Koss et al., 2016). Different from H₃O⁺ PTR-ToF-MS by which the sensitivity for a given ROG can be calculated theoretically even without the standard for calibration, authentic standards are necessary for quantification by NO⁺ PTR-ToF-MS, which limited the characterization of mass spectrum ionized by NO⁺. The difficulty to predict the ionized ROG products and to interpret the mass spectrum unambiguously further limited its application in ROG speciation, because NO⁺ has three common reaction mechanisms with ROGs: charge transfer, hydride abstraction, and cluster formation (Koss et al., 2016). Therefore, NO⁺ PTR-ToF-MS in this study was only used for a supplementary measurement of higher alkanes (\geq C8) with a well-established quantitative method (Wang et al., 2020a).

C8-C15 alkanes were calibrated using a custom cylinder (Linde Gas North America LLC, USA) and sensitivities of C16-C21 alkanes were assumed to be the same as that of C₁₅ n-alkane according to Wang et al. (2022) (Wang et al., 2020a). The uncertainty caused by this assumption was negligible because the degree of fragmentation, a parameter inversely proportional to the sensitivity of higher alkanes, was similar between C16-C21 alkanes and C15 alkanes (~20%) (Wang et al., 2020).

(ii) GC-MS/FID

Against the limitations of PTR technologies (Arnold et al., 1998; Gueneron et al., 2015), GC-MS/FID with a cryogen-free preconcentration device was also deployed. Fifty-seven hydrocarbons and 12 oxygenated organic compounds were measured by GC-MS/FID and quantified using gas standards (Linde gas North America LLC, USA).

(iii) Overlapping species

Thirty-two species measured by GC-MS/FID overlapped the 14 protonated ions measured by H₃O⁺ PTR-ToF-MS (the pink shadow bar in Fig. R3), including 16 aromatic hydrocarbons, 10 carbonyls and 6 Biogenic Volatile Organic Compounds (BVOCs), denoting the species generally emitted and formatted from natural sources in atmosphere. The concentrations of overlapping species in all samples were carefully compared and showed good consistencies between two instruments (slope = 1.00 ± 0.15 , $0.94 < r < 0.99$) (Fig. S5). Considering the better performance of GC-MS/FID in isomer differentiation, GC-MS/FID data were given precedence.

Although C8-C10 alkanes were measured by both GC-MS/FID and NO⁺ PTR-ToF-MS, they represent different meanings. The concentration of higher alkanes from NO⁺ PTR-ToF-MS should be regarded as the summed concentrations of n-alkanes and branched alkanes that have the same chemical formulas. C8-C10 alkanes measured by GC-MS/FID were mainly normal alkanes and few branched alkanes. Following the principle of maximizing the species conservation, the GC data was used to preserve isomer speciation. Meanwhile, after subtracting the concentrations of relevant GC species, the NO⁺ PTR-ToF-MS data was also remained as an independent species.

(iv) Formaldehyde

Formaldehyde, a very important species from combustion (Zarzana et al., 2017) but not measured in this study (Section 2.2.4), was assumed to account for ~7% and ~5% in all discussed species for coal and biomass combustion in this study, respectively, according to the previous reported results (Cai et al., 2019; Stockwell et al., 2015; Stockwell et al., 2016). Specifically, the emission ratio of formaldehyde ($ER_{\text{HCHO,ref}}$) to benzene from anthracite coal (2.13 g/g, benzene) and straws (2.85 g/g, benzene) combustion could be obtained from Cai et al. (2019) and Stockwell et al. (2016). Benzene was chosen for normalization because in the emissions of all types of fuel combustion, benzene was the most abundant aromatics that were the major overlapping species between the current and previous studies. Considering the emission ratios of the species covered by both previous studies and the current work were in good agreement as shown in Fig. S6, the mass fraction of formaldehyde ($f_{\text{HCHO,cal}}$) in ROG emissions from combustion of this work could be calculated using the previously reported $ER_{\text{HCHO,ref}}$ and the currently measured mass fraction of benzene (f_{benzene}) as follows:

$$f_{\text{HCHO,cal}} = \frac{ER_{\text{HCHO,ref}} \times f_{\text{benzene}}}{1 + ER_{\text{HCHO,ref}} \times f_{\text{benzene}}} \quad (\text{R1})$$

Finally, all the species included in this study were sketched in Fig. R3 (Fig. 2 in the main text), as well as their mass fractions in ROG emissions from residential combustion which would be discussed in detail below. Combining 965 unique masses detected by H_3O^+ PTR-ToF-MS with 69 species detected by GC-MS/FID, 14 higher alkanes detected by NO^+ PTR-ToF-MS, as well as formaldehyde from references, a total of 1049 species were used in this study, including 27 alkanes, 9 alkenes, 1 alkyne, 16 aromatics, 6 BVOCs, 9 Polycyclic Aromatic Hydrocarbons (PAHs), 14 higher alkanes, 16 carbonyls, 10 furans (furan and its homologues and derivatives), 9 phenols (phenol and its homologues and derivatives), 8 nitrogen-containing species and 924 other species with large uncertainty. Among them, only 125 species with uncertainty below 50% were included in the speciation of ROG from residential combustion emissions. Table S2 in the Supplementary Information listed the 125 species and their uncertainties. They contributed $89\% \pm 20\%$ and $92\% \pm 34\%$ of the total ROG from residential combustion.

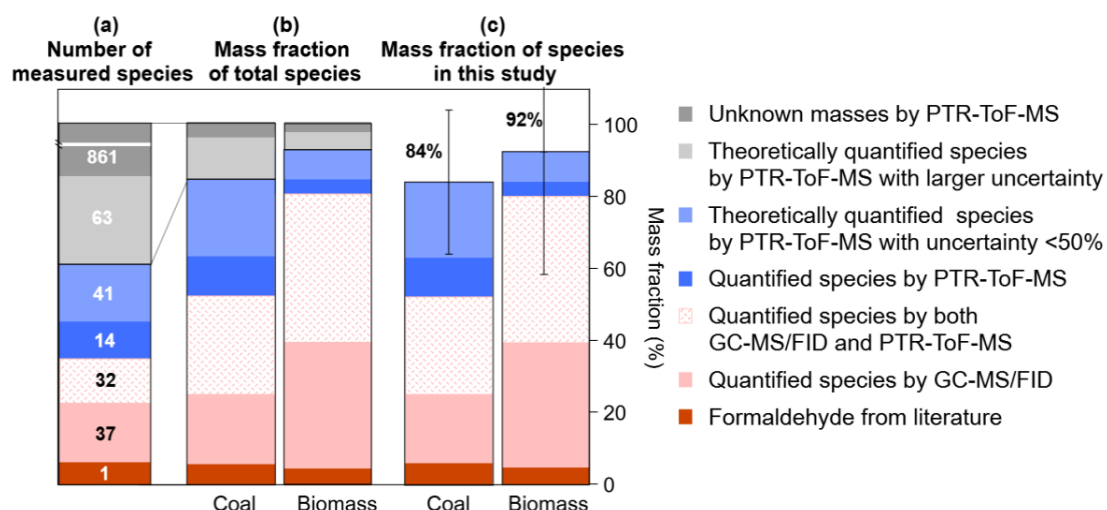


Figure R3. The number and mass fraction of species measured in this study. (a) The number of measured species. (b) The average mass fraction of all measured species from coal combustion and biomass combustion. (c) The mass fraction of selected 125 species in ROGs measured in this study.

The result of formaldehyde was cited from previous studies (Cai et al., 2019; Stockwell et al., 2015). All the quantified species were calculated by standard matters. The theoretically quantified species without available standards were measured by H_3O^+ PTR-ToF-MS by the calculation method proposed by Sekimoto et al. (2017) to determine the relationship between ROG sensitivity and kinetic rate constants for proton transfer reactions of H_3O^+ with ROGs. Among the above theoretically quantified species, species like alcohols and acids (-OH and -COOH), species with more than 2 oxygen atoms (usually 2 functional groups) and components containing $-\text{NO}_n$, had relatively large uncertainty due to the potential loss in the storage. The unknown species were detected by H_3O^+ PTR-ToF-MS and were semi-quantified by the sensitivity of acetone.

We have revised the description of measurement methods in detail in Section 2.2 and Section 2.3 in the revised manuscript.

Q4: Line 122.... assuming all the signals with the same sensitivity as acetone. Does this assumption stand, since acetone has a higher proton affinity than many VOC compounds.

R:

It should be clarified that the sensitivity of acetone was employed as a proxy only for the 861 unknown masses measured by H_3O^+ PTR-ToF-MS in this study. Acetone has been the preferred choice for sensitivity substitutes of other species (Cai et al., 2019) due to its humidity independence (De Gouw and Warneke, 2007). Acetone was also used in this study to keep consistent with previous studies. As the reviewer mentioned, the proton affinity and the kinetic reaction rate constant (k_{kinetic}) of acetone are 812 kJ mol^{-1} and $3.23 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ respectively, higher than those of ~80% of species in Cappellin's study on k_{kinetic} (Cappellin et al., 2012). Thus, the upper limit to the sensitivity was generally provided for unknown species (Koss et al., 2018). For unknown masses, the uncertainty was mainly from the difference of their "real" sensitivities from the assumed sensitivity of acetone, which was dependent on the difference of their k_{kinetic} . Generally, the oxygenated species ($\text{C}_x\text{H}_y\text{O}_z$) have higher ($\sim 2.5\text{--}3.5 \times 10^{-9} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) k_{kinetic} than those of aliphatic hydrocarbons (C_xH_y , $\sim 2 \times 10^{-9} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$), and the k_{kinetic} of acetone is $3.23 \times 10^{-9} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (Cappellin et al., 2012). Thus, the maximum uncertainty of the estimated concentrations of unknown masses caused by this assumption is estimated to be 65% although the "real" k_{kinetic} is as low as $2 \times 10^{-9} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ in this study.

The reason for using the sensitivity of acetone and the potential uncertainty has been added in Section 2.2.3 of the main text.

"Estimation method (861 masses). For unknown masses, it is difficult to estimate k_{kinetic} which depends on molecular properties, and the sensitivity of acetone was used as a proxy (Cai et al., 2019).

...For unknown masses, the uncertainty was mainly from the difference of their "real" sensitivities from the assumed sensitivity of acetone, which was dependent on the difference of their k_{kinetic} . Generally, the oxygenated species ($\text{C}_x\text{H}_y\text{O}_z$) have higher ($\sim 2.5\text{--}3.5 \times 10^{-9} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) k_{kinetic} than those of aliphatic hydrocarbons (C_xH_y , $\sim 2 \times 10^{-9} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$), and the k_{kinetic} of acetone is $3.23 \times 10^{-9} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (Cappellin et al., 2012). Thus, the maximum uncertainty of the estimated concentrations of unknown masses caused by this assumption is estimated to be 65% although the "real" k_{kinetic} is as low as $2 \times 10^{-9} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ in this study."

Q5: Line 169 why is formaldehyde not reported in your study since PTR ionize formaldehyde efficiently.

R:

Formaldehyde, a special species during PTR measurement was not detected in this study, suffering from double effects by (1) mass discrimination and (2) reversible reaction.

(1) Mass discrimination

For the PTR-ToF-MS deployed in this study, as the transmission curve (Fig. S2) shows, the mass transmission efficiency of protonated formaldehyde at m/z 31 is close to 0, leading to an almost negligible sensitivity of formaldehyde. The decisive factor for transmission efficiency of PTR-ToF-MS is the radio frequency (RF) amplitude and the frequency of the big segmented quadrupole (BSQ), which can be set up as an ion filter (Wang et al., 2020c). A similar situation has been reported by Yang et al. (2022), in which formaldehyde was not measured by the PTR-ToF-MS (Vocus 2R, Aerodyne Research Inc.) (Yang et al., 2022).

(2) Reversible reaction

Non-negligible back reactions between protonated formaldehyde and water vapor can reduce the sensitivity for formaldehyde (Spanel and Smith, 2008; Cui et al., 2016). For the developed Vocus instrument deployed in current work, the water vapor flow increases from the previous level 4–8 sccm ($\text{cm}^3 \text{min}^{-1}$ at 105 Pa and 273.15 K) (De Gouw et al., 2004) to 20–30 sccm (Krechmer et al., 2018). This change brings a great advantage that the humidity dependence of instrument response to most species can be ignored. However, for formaldehyde, the reduction of its sensitivity is predictable because the really high water vapor concentration was provided for the back reactions.

We have clarified it more clearly in Section 2.2.4 in the revised manuscript.

Q6: Line 255 figure 2. What is the x-axis label, m/z or numbers of identified species. Add x-axis label.

R:

The x-axis label “Numbers of identified species” was added at the bottom of Fig. R4 (**Fig. 3 in the revised main text**). An additional explanation of x axis was provided in the title of Fig. R4, that is “The identified species corresponding to the numbers of x axis are listed in Table S2 in the Supplementary Information”.

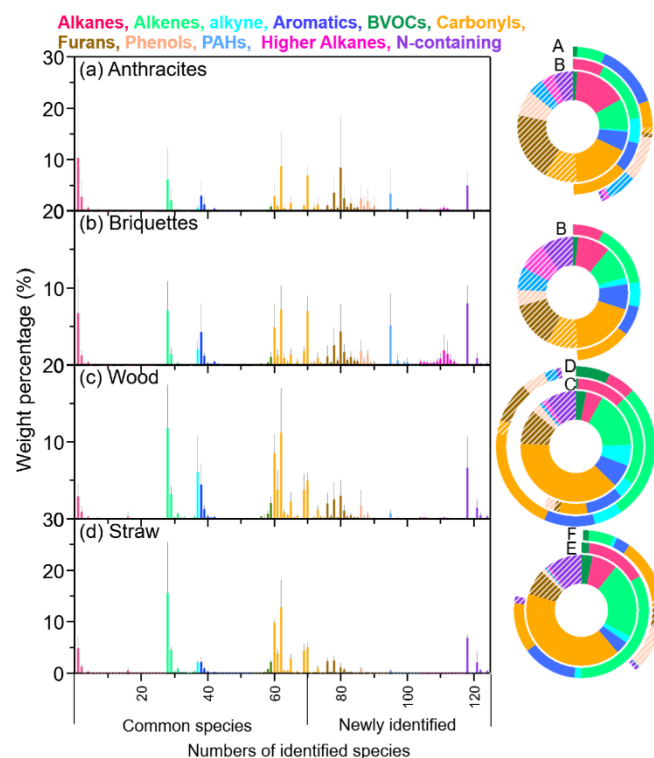


Figure R4. Source profiles and compositions of the four types of residential fuels including (a) anthracites, (b) briquettes, (c) wood and (d) straws (average of corncob, bean straws and corn straws) as well as those of the previous results. A. anthracites combustion in stove from Cai et al., 2019 (Cai et al., 2019); B. residential coal combustion simulation in lab from Mo et al., 2016 (Mo et al., 2016); C. hardwood combustion simulation in lab from Stockwell et al., 2016 (Stockwell et al., 2016); D. Black Spruce combustion simulation from lab experiments reported by Hatch et al., 2017 (Hatch et al., 2017); E. wood combustion simulation from Wang et al., 2014 (Wang et al., 2014); F. rice straw combustion simulation from Stockwell et al., 2015 (Stockwell et al., 2015). The identified species corresponding to the numbers of x axis are listed in Table S2 in the Supplementary Information. The shaded parts of pie charts represent the newly identified species.

Technical corrections:

Line 73, 276, 320, 360 space missing before the left bracket.

R:

Space was added before the left bracket as suggested.

Line 94 “particles was” should be “particles were”

R:

Revised as suggested.

Line 97 space missing before „f.

R:

Space was added before “°C” as suggested.

Line 100 there were 23 samples were collected, grammatical mistake

R:

This sentence has been revised to the following statement:

“Here totally 23 samples were collected, as shown in Fig. S1”.

Line 130 space missing before the left bracket.

R:

Revised as suggested.

Line 135 10 carbonyls are included in Table S2.

R:

In the original manuscript, 12 carbonyls were measured by GC-MS/FID. Among them, as the reviewer mentioned, 10 carbonyls were listed in the category “Carbonyls” in Table S2. It should be noted that the other 2 carbonyls including methacrolein and methyl vinyl ketone were classed into Biogenic Volatile Organic Compounds (BVOCs) in Table S2.

To avoid ambiguity, we revised “carbonyls” in the main text into “oxygenated organic compounds”:

“Fifty-seven hydrocarbons and 12 oxygenated organic compounds were measured by GC-MS/FID and quantified using standard gases (Linde gas North America LLC, USA).”

Line 137 delete including 68 species.

R:

Revised as suggested.

Line 185 add a space before and after and check throughout the whole manuscript.

R:

All issues related to space missing were checked and revised throughout the whole manuscript as suggested.

Line 211 as → that

Line 227 as Fig. 2(c) shown → as shown in Fig. 2(c) or as Fig. 2(c) showed/shows.

R:

Revised as suggested.

Line 251 253 two types of data format shown, i.e., $\text{xxx}\% \pm \text{xxx}\%$ or $\text{xxx} \pm \text{xxx}\%$. Check throughout the whole manuscript keep consistency.

R:

The data format was checked and unified to one type throughout the whole manuscript.

Line 276, according SOA yields → respective SOA yields.

R:

Revised as suggested.

Line 351, due to is a preposition and should not a complete sentence.

R:

“due to” was replaced by “because”.

Line 354, comparing with → compared with

Line 357, 2017 benefiting → 2017, benefiting

Line 397, in rural of China → in rural China

R:

Revised as suggested.

I believe the above technical corrections are not complete, authors should check carefully.

R:

The technical details and grammar have been checked and revised carefully throughout the whole manuscript.

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