Measurement report: Underestimated reactive organic gases from residential combustion: insights from a near-complete speciation

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Abstract

Reactive organic gases (ROGs), as important precursors of secondary pollutants, are not well resolved as the chemical complexity challenged its quantification in many studies. Here, a near-complete speciation of ROGs with 125 species was developed and applied to evaluate their emission characteristics from residential solid fuel combustion. ROGs identified by the present method accounted for ~90% of the “total” as the sum of species by Gas Chromatography equipped with a Mass Spectrometer and a Flame Ionization Detector (GC-MS/FID) and H₂O⁺/NO⁺ Proton Transfer Reaction Time-of-Flight Mass Spectrometer (Vocus PTR-ToF-MS). The study further revealed that with 55 species, mainly oxygenated species, higher hydrocarbons with > 8 carbon atoms, and nitrogen-containing ones, previously un- and under-characterized, ROG emissions from residential coal and biomass combustion were underestimated by 44.3% ± 11.8% and 22.7% ± 3.9%, respectively, which further amplified the underestimation of secondary organic aerosols formation potential (SOAP) as high as 70.3% ± 1.6% and 89.2% ± 1.0%, respectively. The OH reactivity (OHR) of ROG emissions was also undervalued significantly. The study highlighted the importance of acquiring
completely speciated measurement of ROGs from residential emissions, as well as other processes.

Highlights

A near-complete speciation of ROGs emitted from residential combustion was developed.

Oxygenated species, higher hydrocarbons and nitrogen-containing ones played larger roles in the emissions of residential combustion comparing with the common hydrocarbons.

ROG emissions from residential combustion were largely underestimated, leading more underestimation of their OHR and SOAP.

Keywords: Chemical speciation, Reactive organic gases, Residential combustion, Estimation bias
1. Introduction

Residential combustion, dominated by approximately 89% solid fuels in China (Zhu et al., 2019), is responsible for ~23% and ~71% of the outdoor and indoor PM$_{2.5}$ concentrations, and ~67% of PM$_{2.5}$-induced premature deaths (Yun et al., 2020). Reactive organic gases (ROGs), organic gases other than methane, from residential combustion, have been shown to serve as key precursors for secondary organic aerosols (SOA) (Huo et al., 2021) and ozone formation (Heald and Kroll, 2020; Heald et al., 2020). Recommended 56 hydrocarbon species according to the Photochemical Assessment Monitoring Station (PAMS), the most common ROG species, have been recognized as the dominant ROGs from residential combustion in past years (Mo et al., 2016). With the development of advanced detection technologies, more ROGs like oxygenated volatile compounds (OVOCs) and higher alkanes with carbon atoms more than 12, have been found to play important roles in the source emissions as well as in the atmospheric chemistry (Yuan et al., 2017; Wang et al., 2020a; Chang et al., 2022; Gao et al., 2022; Wang et al., 2022; Qu et al., 2021). A more complete chemical description of ROGs emitted from residential coal and biomass combustion was critically important to get more insights into their atmospheric effects.

Several studies attempting complete identification and quantification of ROGs mainly emitted from biomass combustion have been conducted in the laboratory using multiple trace-gas instruments in recent years (Gilman et al., 2015; Hatch et al., 2017), which have mainly focused on emissions from various trees and other wildfire fuels. Andreae (Andreae, 2021, 2019) summarized the ROG speciation and emission factors of various kinds of combustion processes and concluded there were lack of results from actual combustion processes like in field or household combustion and species such as higher alkanes serving as important SOA precursors were not included in the previous studies (Table S1)(Koss et al., 2018; Cai et al., 2019).

In this study, the ROGs emitted from typical Chinese household stoves with six kinds of solid fuels were analyzed with the combination of a high mass resolution Vocus Proton Transfer Reaction Time-of-Flight Mass Spectrometer (Vocus PTR-ToF-MS) under two kinds of ion source (H$_3$O$^+$ / NO$^+$) and a gas chromatography system equipped with a mass spectrometer and a flame ionization detector (GC-MS/FID). The Vocus
PTR-ToF-MS have a good sensitivity for most of OVOCs and aromatics as well as some nitrogen-/sulfur-containing species in the mode of H3O+ (Wu et al., 2020), and for higher alkanes in NO+ mode (Wang et al., 2020a). GC-MS/FID has a wide detection range of organics, and here is used for the detection of nonmethane hydrocarbons (NMHCs) and some carbonyls. Accordingly, a near-complete speciation of ROGs including 125 species results from the combined instrument data sets, further supporting the evaluation of the roles of ROG emissions from residential combustion in the formation potential of SOA and ozone in China.

2. Materials and methods

2.1 Sampling

The ROG samples of the combustion of four typical biomass fuels (wood, corncob, bean straw and corn straw) and two typical coals (anthracite, and briquette coals) (see Fig. S1) were collected from the stack nozzles of household stoves by vacuumed SUMMA canisters (Entech Inc., 3.2 L). During canister sampling, the combustion in the stoves was in the stage of flaming visually, which was the common condition for heating or cooking in the rural areas in northern China. Particles was removed by a particle-filter with 5.0 μm pore size Teflon filter (PTFE). Temperatures (37 ± 17 °C) of flue gas were monitored at the sampling location by a flue gas analyzer (Testo 350). Wood and straws burned at an average temperature of 394°C (in the range of 231°C–567°C) and 353°C (334°C–371°C), respectively, while the residential coals burned at a higher temperature (514°C, 411°C–581°C), which were measured by an infrared thermometer in the stove. There were 23 samples were collected in all in this study, as shown in Fig. S1.

2.2 Analysis

All the samples stored in SUMMA canisters were detected with the combination of Vocus PTR-ToF-MS (Vocus 2R, Tofwerk AG, Switzerland) and GC-MS/FID (TH-300, Wuhan Tianhong Instruments, China) within 9 days. The effect of storage inside the canister was evaluated using the standard samples with different storage duration in the laboratory. The intercomparisons of different methods were carried out to ensure the results were comparable. Accordingly, the measurement uncertainties of different
ROG species were estimated, as listed in Table S2. Details of the measurements were as following.

**PTR-ToF-MS.** A commercial Vocus PTR-ToF-MS with H$_3$O$^+$ and NO$^+$ chemistry was used to detect ROGs. The Vocus PTR-ToF-MS was operated at a mass resolving power of 10000 m $\Delta$m$^{-1}$ (full width at half maximum, FWHM). A total of 1005 peaks were extracted from raw spectral data by Tofware package v3.2.3 (Tofwerk Inc.), including all peaks with mass to charge ratio (m/z) below 200 under H$_3$O$^+$ mode and selected peaks under NO$^+$ mode (mainly higher alkanes). The peak assignment was derived based on accurate m/z values, isotopic patterns and previous study results (Pagonis et al., 2019). In all, 162 ions with a relative high degree of certainty associated with previous reports (Pagonis et al., 2019; Cai et al., 2019; Koss et al., 2018) were identified and had noticeable concentrations in the samples. These 162 masses represent about 89% of the total extracted signal measured by Vocus PTR-ToF-MS, assuming all the signals with the same sensitivity as acetone. Twenty-six out of 162 identified species were calibrated using customized cylinders (Linde Gas North America LLC, USA) including benzene, toluene, styrene, m-xylene, 1,3,5-trimethylbenzene, isoprene, alpha-pinene, methyl vinyl ketone, naphthalene, acrolein, acetone, methyl ethyl ketone, 2-pentanone, acetaldehyde, furan, acetonitrile, dichlorobenzene, ethyl acetate and C$_8$–C$_{15}$ n-alkanes. More details of the calibration could be found in our previous studies (Gao et al., 2022; Wang et al., 2020b). Sensitivities of C$_{16}$–C$_{21}$ alkanes were assumed to be same as that of C$_{15}$ n-alkane according to Wang et al. (2022) (Wang et al., 2020a). For other measured species, we used the method proposed by Sekimoto et al. (2017) to determine the relationship between ROG sensitivity and kinetic rate constants for proton transfer reactions of H$_3$O$^+$ with ROGs (Fig. S2), and the uncertainties of the concentrations for these uncalibrated species were about 50% (Table S1) (Sekimoto et al., 2017).

**GC-MS/FID.** 57 NMHCs and 11 carbonyls were detected by GC-FID/MS coupled with a cryogen-free preconcentration device, which were calibrated by gas standards (Linde Gas North America LLC, USA) including 68 species as listed in Table S2. Intercomparisons between GC-FID/MS and Vocus PTR-ToF-MS for overlapped ROG species were carefully evaluated. Good agreements for aromatics and some
carbonyls were observed in all samples (Fig. S3).

**Loss in storage.** To determine the possible artifacts caused by the SUMMA canister storage, standard samples with concentration of 5 ppbv containing 81 species 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. The detailed compounds and deviations were shown in Table S2 and Fig. S4. Generally, on the 10th day, the relative deviations were within 20% for 71 out of the 81 standard compounds, and the rest 10 compounds like diethylbenzene, terpenoids and long-chain alkanes had the relative deviations within 49%. The concentration of the standard sample was lower than most of the concentrations of species in source samples. Thus, the estimated loss in the storage in this study was the upper bound for the source samples. For acids and alcohols with larger loss in the canisters potentially due to the functional groups of -COOH and -OH, the measured concentrations in the samples were excluded from the results, and especially there were no standard gases used to evaluate the loss during storage. The estimated total uncertainty of ROGs were in the range of 4%–50%, which included the uncertainties of storage and detection, as listed in Table S2.

**Speciation.** Finally, 87 out of the 162 species measured by Vocus PTR-ToF-MS were used in this study, including 31 overlapped species with those by GC-FID/MS (Fig. 1). Since isomers can’t be distinguished by Vocus PTR-ToF-MS, GC-FID/MS measured concentrations for overlapped ROG species were used in this study. Combining with other 37 species detected by GC-MS/FID, a total of 124 species were used in this study, including 27 alkanes, 9 alkenes, 1 alkyne, 16 aromatics, 6 biogenic volatile organic compounds (BVOCs), 9 polycyclic aromatic hydrocarbons (PAHs), 14 higher alkanes, 15 carbonyls, 10 furans (furan and its homologues and derivatives), 9 phenols (phenol and its homologues and derivatives) and 8 nitrogen-containing compounds. Other species detected by Vocus PTR-ToF-MS but not included in the follows were mainly acids, alcohols and species with more than 2 oxygen atoms, accounting for about 8% (ranging from 2% to 17% in different samples) of the total ROG masses as shown in Fig. S5.

**Formaldehyde,** a very important species from combustion (Zarzana et al., 2017) but not measured in this study, 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_{HCHO,ref}) from anthracite coal combustion (2.13 g/g benzene) and straws (2.85 g/g benzene) could be obtained from Cai et al. (2019) and Stockwell et al. (2016). Considering the emission ratio of the species covered by both previous studies and the current work were consistent as shown in Fig. S6, the mass fraction of formaldehyde (f_{HCHO,cal}) in ROG emissions from coal combustion of this work could be calculated using the previously reported ER_{HCHO,ref} and the currently measured mass fraction of benzene (f_{benzene}) as follows:

\[
f_{HCHO,cal} = \frac{\text{ER}_{HCHO,ref} \times f_{benzene}}{1 + \text{ER}_{HCHO,ref} \times f_{benzene}}
\]

Finally, all the species included in this study were sketched in Fig. 1, as well as their mass fractions in ROG emissions from residential combustion which would be discussed in detail below. Briefly, although only 125 out of more than 1000 species were included in the speciation of ROGs from residential combustion emissions, they have contributed 89±20% and 92±11% of the total ROGs from residential combustion.

Figure 1. The number and mass fraction of species measured by GC-MS/FID and Vocus PTR-ToF-MS. (a) Number of measured species by GC-MS/FID and Vocus PTR-ToF-MS. (b) Average mass fraction of all measured species from coal combustion and biomass combustion samples. (c) Mass fraction of selected 125 species 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 semiquantified species were measured by Vocus PTR-ToF-MS (H$_3$O$^+$) by the method proposed by Sekimoto et al. (2017) to determine the relationship between ROG sensitivity and kinetic rate constants for proton transfer reactions of H$_3$O$^+$ with ROGs. Among the above semiquantified species, species with the functional groups of -OH and -COOH as well as those with more than two oxygen atoms had relatively large uncertainty due to the potential loss in the storage. The unknown species were detected by Vocus PTR-ToF-MS (H$_3$O$^+$) and were semiquantified by the sensitivity of acetone.

3. Results and discussions

3.1 A near-complete speciation of ROGs from residential combustion

ROG compositions emitted from typical residential combustion using two types of coals (anthracite, and briquettes) and four types of biomasses (wood, corncob, corn straw and bean straw) are shown in Fig. 2. The measured ROG profiles for each kind of fuel had a good correlation (R > 0.6) (Fig. S7), and the average result was used here. Generally, ROGs emitted from the residential combustion can be divided into three groups based on the element composition, including hydrocarbons, oxygenated species, and nitrogen-containing species. Differing from the previously studies which mainly stressed the dominant role of hydrocarbons (Mo et al., 2016; Stockwell et al., 2015; Wang et al., 2014), the contribution of oxygenated species (36.8%–56.8%) was comparable with that of hydrocarbons (40.8%–48.7%) in this study. It was expected as 24 more oxygenated species mainly including furans, phenols and carbonyls were measured by Vocus PTR-ToF-MS in our study, which were un- and under-characterized in previous studies using GC methods. Besides hydrocarbons and oxygenated species, nitrogen-containing species mainly included acetonitrile and acrylonitrile also played a considerable role in ROG emissions from residential combustion, with the proportions ranging from 5.7% to 14.5%, which have been previously reported (Cai et al., 2019).

Here, we defined the species previously un- and under-characterized by GC methods as newly identified species and could be measured only using Vocus PTR-
ToF-MS in this study, and as a result 55 of 125 species were newly identified species. As shown in Fig. 2, these newly identified species mainly including furans and phenols contributed 44.3% ± 11.8% of the total ROGs for coal emissions and 22.7% ± 3.9% of the total ROGs for biomass emissions. We also compared our results with the previous reports, and for comparison the previous speciation was scaled by the total fraction of the previously reported species in the total ROGs measured in this study. As shown in Fig. 2 and Fig. S5, the fraction of reported species in previous studies was comparable to the present result. In particular, as Fig. 2(c) shown, the present composition of ROGs from residential wood combustion was close to that of Black Spruce combustion simulated in laboratory by multiple advanced trace-gas instruments, which reported 464–551 species (~173 molecules) in all (Hatch et al., 2017). It further confirmed that the obtained ROG characterization with the combination of Vocus PTR-ToF-MS and GC-FID/MS were nearly complete. Our study underscored the importance of the completely speciated measurement of the ROG emissions from residential combustion especially for coal combustion.

Large difference was observed between the ROG speciation of coal and biomass combustion but not significant among different types of coal or biomasses, as shown in Fig. 2. Specifically, the alkenes mainly ethylene and propene dominated hydrocarbons emitted from biomass combustion, while alkanes were the most hydrocarbons from coal combustion. Especially, coal combustion emitted considerable higher alkanes including 8–21 carbon atoms and gaseous PAHs (mainly including 2–3 benzene rings), primarily generated by pyrolysis of the volatile matter in coal (Du et al., 2020), accounting for 8.3%–14.8% of ROGs much higher than the minor fractions (0.4%–2.4%) for biomass combustion emissions. In terms of oxygenated species, coal combustion emitted considerable furans (16.8% ± 3.2%) and phenols (6.1% ± 1.5%) mainly formed through pyrolysis of polymers in coal (Liu et al., 2017; Morgan and Kandiyoti, 2014), which together played a comparable role with carbonyls (26.9% ± 6.8%) in ROGs. In comparison, carbonyls (40.6% ± 6.6%) were the dominant oxygenated species in ROG emissions from biomass combustion, mainly originated from products of biomass pyrolysis and pyrosynthesis (Morgan and Kandiyoti, 2014). A slightly higher
proportion of phenols and furans from wood combustion (12.8% ± 3.0%) than straw combustion (8.7% ± 2.8%) were observed, possibly resulting from the higher composition of lignin in wood (Collard and Blin, 2014). Considerable terpenes were also observed in ROG emissions from residential coal (1.5 ± 0.2%) and biomass (3.2% ± 0.5%) combustion.

![Figure 2](https://example.com/figure2.png)

**Figure 2.** 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; B. residential coal combustion simulation in lab from Mo et al., 2016; C. hardwood combustion simulation in lab from Stockwell et al., 2016; D. Black Spruce combustion simulation from lab experiments reported by Hatch et al., 2017; E. wood combustion simulation from Wang et al., 2014; F. rice straw combustion simulation from Stockwell et al., 2015 (Cai et al., 2019; Mo et al., 2016;
Wang et al., 2014; Stockwell et al., 2016; Hatch et al., 2017; Stockwell et al., 2015). The measured species corresponding to the numbers of horizontal axis are listed in Table S2. The shaded parts of pie charts represent the newly identified species.

3.2. SOAP and OHR underestimation from newly identified species

To further understanding the role of residential combustion emitted ROGs in atmospheric chemistry, the OH reactivity (OHR) and formation potential (SOAP) of per unit mass (or concentration) of ROGs emitted from residential combustion was calculated based on the source profiles. OHR is defined here as the sum of OH reactivity of each species, calculated by product of ROG species weight percentage ($W_{ROG_i}$) in emissions from residential combustion and corresponding OH reaction rate ($k_{OH+ROG_i}$) (Carter, 2008; Koss et al., 2018), as presented in Eq. (2) below. SOAP is the sum of SOAP of each species and calculated by multiplying proportion of ROG species with according SOA yields based on the reported approach (Ng et al., 2007; Lim and Ziemann, 2009), as presented in Eq. (3) below.

$$\text{OHR} = \sum W_{ROG_i} \times k_{OH+ROG_i}$$  \hspace{1cm} (2)

$$\text{SOAP} = \sum W_{ROG_i} \times \text{Yield}_{ROG_i}$$  \hspace{1cm} (3)

Figure 3 shows the OHR and SOAP of per unit mass (or concentration) ROG emissions. The OHR for coal and biomass emissions were quite similar (0.14–0.16 s$^{-1}$ µg$^{-1}$ m$^3$) but with different compositions, which was expected as the differences of their ROG compositions. The OHR was dominated by oxygenated species (39.6%–73.7%) and alkenes (15.0%–48.2%), and the contribution of other species was within the range of 9.3%–17.1%. The newly identified ROG species dominated the OHR of coal combustion with the fractions of 64.2% ± 7.8% and 54.6% ± 9.3% for anthracites and briquettes combustion, respectively, due to the large contribution of furans, phenols, PAHs, and higher alkanes in ROGs. In comparisons, the previously reported species contributed more to OHR of biomass combustion than that of newly identified species. The ratio of OHR between newly identified and previously reported ROGs was 1.20–1.80 for coals and 0.22–0.51 for biomass, much higher than the ratios of their emissions (0.79–0.81 for coals and 0.20–0.36 for biomass). It meant that the OHR of ROG emissions from residential coal and biomass combustion was underestimated by 59.4%.
± 4.8% and 26.2 ± 6.8%, respectively, without the newly identified species. SOAP derived from per unit mass ROG emissions of coal combustion was 0.078–0.085 μg μg⁻¹, much higher than that from biomass combustion (0.016–0.035 μg μg⁻¹). Nevertheless, for all samples, newly identified ROGs accounted for over 70% of the SOAP. SOAP was dominated by newly identified oxygenated species like phenols which contributed 47.6% ± 12.4% and 56.7% ± 7.0% to SOAP of emissions from coal and biomass combustion, respectively, and higher alkanes and PAHs also played important roles in SOAP emissions from coal combustion. The ratios of SOAP derived from newly identified ROGs and previously reported ROGs were 7.8–8.8 and 2.2–2.7 for coals and biomass, respectively, much higher than those of mass percentages. These results indicated that for both coal and biomass combustion, the measurement of newly identified ROGs would be greatly affected on SOA estimation. The field study has found that newly identified ROGs like higher alkanes and PAHs contributed more than 60% of SOA formation from measured precursors in ambient air (Wang et al., 2020a). Our study of ROG emissions could donate to the explanation of the high SOA formation in atmosphere to some extent. In other words, failure to include newly identified ROGs in emission inventories and SOA models could lead to significant underestimation of residential contribution to SOA production.

Figure 3. OH reactivity and SOA formation potential (SOAP) of per unit mass (or concentration) of ROG emissions for coal and biomass combustion. The shaded parts
3.3 ROG emissions from residential combustion in China

ROG emissions could generally be calculated through multiplying the activity data by the emission factors which were not measured in this study. However, the emission factors of most of the common ROGs like hydrocarbons in the emissions from residential combustion have been reported in previous studies (Cai et al., 2019; Stockwell et al., 2015). Hence, the emission factor of the newly identified ROG species in this study could be estimated by the reported emission factor (EF) of the previously reported species combining with their emission ratio (ER) in residential combustion. Here, the benzene as well as its reported EF was used for the purpose above, and we also tested other species with reported EFs (Fig. S8). There were no significant differences (-39%–4% for straws and 6%–26% for coals) of the estimated EFs of newly identified ROGs among different tests, which further confirmed our results were comparable with the previous studies but with more ROG species measured, as shown in Fig. S8. The ER of other ROG species to benzene was the ratio of their concentrations in the sample, and the average ER in different samples of each type of fuel was used in this study, as listed in Table S3. Notably, the EFs of anthracite and straw combustion were used below to estimate the ROG emissions of residential coal and straw combustion in China mainland.

Accordingly, the national ROG emissions of residential combustion were estimated combining with the residential coal consumption and the crop straw combustion data in China. Specifically, the data of residential coal consumption from 2010 to 2019 were from the China Energy Statistical Yearbook (National Bureau of Statistics, 2010-2022), which included the data of each province in China mainland in each year. The data of crop straw combustion from 2010 to 2019 (Table S4) were from Report of Prospects and Investment Strategy Planning Analysis on China Straw Refuse Treatment Industry (2022-2027) (Qianzhan Industrial Research Institute, 2022), which only reported the total amount of the whole China mainland and included both the household and field combustion. The province data of crop straw combustion in 2017 (Table S5) were used to study the spatial distribution in this study, which were from Second National Pollution Source Census Bulletin (Ministry of Ecology and Environment of the People's
The spatial and temporal distribution of ROG emissions from residential combustion was presented in Fig. 4. The total emissions of ROGs from residential coal combustion and crop straw combustion were 14 kt and 4384 kt in 2019, respectively, and as expected these values were underestimated by 44.3% ± 11.8% and 22.7% ± 3.9%, respectively, due to fewer species were included previously. Unexpectedly, the ROG emissions from crop straw combustion were two orders of magnitude higher than those of coal combustion, which included those both from household and field combustion. Notably, the straw combustion emissions were stable after 2017 comparing with the gradual decrease from 2010 to 2017, mainly due to the limitation of straw utilization (Zhu et al., 2019). In comparison, ROG emissions of residential coal combustion began to decrease after 2017 benefiting from the clean heating action in the north of China (National Development and Reform Commission, 2017). Spatially, the hot areas of ROG emissions from residential coal combustion were mainly in the North China Plain (NCP)(Yang et al., 2020), while those of straw combustion were mainly in the main food-production bases of China like the northeastern China, the southern NCP, and Jiangsu, Anhui, and Hunan provinces.
**Figure 4.** Emissions of ROGs from residential coal and straw combustion in China. (a) Annual variation of national ROG emissions and (b) the speciation of ROG emissions in 2019 from residential coal and straw combustion. The black boxes indicate the emissions of newly identified species. (c, d) Spatial distribution of ROG emissions from coal combustion in 2019 and straw combustion in 2017 respectively. The blank parts on the map indicate the provinces with missing data.

### 4. Conclusions

In this study, a near-complete chemical description of ROGs emitted from residential coal and biomass combustion was developed to get more insights into their atmospheric effects. ROGs identified by the present method accounted for ~90% of the “total” as the sum of species by Gas Chromatography equipped with a Mass Spectrometer and a Flame Ionization Detector (GC-MS/FID) and H$_2$O$^+$/NO$^+$ Proton Transfer Reaction Time-of-Flight Mass Spectrometer (Vocus PTR-ToF-MS). Among the near-complete description of ROGs, 55 species un- and under-characterized in previous studies using GC methods were analyzed intensively by Vocus PTR-ToF-MS, mainly including oxygenated species (carbonyls, furans, phenols), higher hydrocarbons (PAHs, higher alkanes) with carbon atoms more than 8 as well as nitrogen-containing compounds.

For the nearly complete ROGs dividing into three categories by the element composition, oxygenated species played a similar major role with hydrocarbons, and nitrogen-containing species dominated by acetonitrile and acrylonitrile were also considerable in ROG emissions from residential combustion. Especially, coal combustion emitted considerable higher alkanes including 8–21 carbon atoms, gaseous PAHs (mainly including 2–3 benzene rings), furans and phenols, differently biomass combustion emitted more carbonyls and terpenes.

Considering the newly discovered species, it is observed that approximately half and a quarter of the ROG emissions from coal and biomass combustion are underestimated. Combining with the spatial-temporal consumption of residential coal and biomass combustion in China, ROG emissions of residential combustion were estimated. The ROG emissions from straw combustion were two orders of magnitude higher than those from coal combustion with negligible decline in recent years as the
limited straw utilization ratio, which suggested the biomass combustion would be the only important residential emissions with the continuous replacement of residential coal in rural of China. Given the newly identified species more reactive or with higher SOA yields, amplified underestimation of OHR and SOAP were observed for both coal combustion (59.4% ± 4.8% and 89.2% ± 1.0%) and biomass combustion (26.2 ± 6.8% and 70.3% ± 1.6%). These results highlighted the importance of the completely speciated measurement of the ROG emissions from residential combustion.

Data availability

Data presented in this paper are freely accessible from the following link:
https://data.mendeley.com/datasets/z78zz7mv7h/1 (Mendeley Data, V1, doi: 10.17632/z78zz7mv7h.1, Wang et al., 2022)

Competing interests

The authors declare that they have no conflict of interest.

Authors contributions. All authors contributed to the manuscript and have given approval of the final version. H.W. and C.H. designed the study. H.W. and Y.G. performed the data analyses and wrote the manuscript. Y.G., L.Y., and S.J. conducted the experiment. B.Y., G.S., Y.L., Q.W., D.H., S.Z., and S.L., contributed to the interpretation of results. L.Z and A.K. revised the manuscript. S.T. assisted in sampling.

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