Aerosol and Air Quality Research

Spatial-temporal Characteristics and Source Apportionment of Ambient VOCs in Southeast Mountain Area of China

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ABSTRACT

Seasonal variations and sources of ambient volatile organic compounds (VOCs) were conducted at the county and rural sites in a mountain area of southeastern China. The results showed that the pattern of VOC concentrations was dominated by oxygenated VOCs (37.6%) and alkanes (25.8%), followed by halocarbons (16.8%), alkenes (11.9%), aromatics (6.87%), and alkynes (1.04%). Based on the OH radical loss rate (L_{OH}) and ozone formation potential (OFP) analysis, alkenes had the highest chemical activity, especially the contribution of isoprene in rural areas. Aromatics contributed the most to secondary organic aerosols (SOA) formation in both county and rural areas. Source apportionment of VOCs were quantified by the positive matrix factorization (PMF) model, including industrial emissions and combustion burning (30.1% and 43.3% in the county and rural areas, respectively) and vehicle exhausts (30.3% and 10.8%), followed by solvent usage (17.1% and 5.2%), liquid petroleum gas (LPG) usage and fuel evaporation (14.2% and 10.0%), and biogenic source (8.3% and 30.6%). The backward air trajectories showed that air mass in spring was mainly originated from the intercity transmission, while the air clusters in autumn came from the northern areas through long-range transport. The study was helpful to understand the pollution characteristics in the mountainous area and provides a scientific basis for local O_3 and $PM_{2.5}$ pollution control.

Keywords: VOCs, Pollution characteristics, Source apportionment, Ozone formation potential, PMF model

1 INTRODUCTION

Air pollutants, including surface ozone (O_3) and fine particulate matter ($PM_{2.5}$), have attracted intense attention worldwide in recent years, which could cause serious adverse effects on air quality, climate change and public health (Mozaffar *et al.*, 2020; Zhan *et al.*, 2021; Zhao *et al.*, 2021). Secondary organic aerosol (SOA) comprises a major fraction of $PM_{2.5}$ and has a driving force in extremely severe pollution episodes (Zhang *et al.*, 2021b). Surviving as important precursors, volatile organic compounds (VOCs) are critical in the formation of O_3 and SOA through atmospheric oxidation and condensation (Zhan *et al.*, 2021; Zheng *et al.*, 2021). However, VOCs have complex components and numerous sources, and the chemical reactivity of each component varies
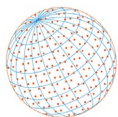
greatly (Hui *et al.*, 2018; Li *et al.*, 2021). Therefore, it is necessary to deeply understand the compositions and reactions with oxidants of VOCs in the atmosphere.

VOCs are emitted from biogenic and anthropogenic sources, such as vehicle emissions, industrial production, the use of various kinds of chemical reagents (such as solvents, coatings, chemical additives), combustion burning, and fuel evaporation (Moreira dos Santos *et al.*, 2004; Yurdakul *et al.*, 2013; Liu *et al.*, 2019; Zhang *et al.*, 2019). Most field campaigns have been conducted in highly urbanized areas due to intensive emission of species with strong atmospheric oxidation capabilities (Dumanoglu *et al.*, 2014; Shao *et al.*, 2016; Zhang *et al.*, 2017; Gao *et al.*, 2018; Kumar *et al.*, 2018; Liu *et al.*, 2019). Other studies set the sampling sites at background areas, focusing on the behaviors of biogenic VOCs (BVOCs) (Zhang *et al.*, 2014; Wu *et al.*, 2016; Matsumoto, 2021). In fact, due to the limited environmental management strategy, many county areas suffer from relatively serious local air pollution problems and also play an important role in the regional transport of air pollutants (Zhang *et al.*, 2019). Nanping city is located in a mountainous area in southeastern China, with high forest coverage and densely distributed small villages. The area is under the East Asian monsoon control, which causes an apparent alternation of polluted and clean air masses from continental and ocean areas, respectively (Hong *et al.*, 2021). Totally, the local geographical environment, including dense vegetation, strong atmospheric oxidation capacity and relatively high humidity, provides a good chance to study the pattern and sources of ambient VOCs, and their contributions to O_3 and SOA formation. With the development of urbanization in these county areas, anthropogenic emissions would be increasingly important to the sources and oxidation capabilities of VOCs. The distribution characteristics and sources of ambient VOCs in the mountainous area might be significantly different from those in developed urban areas.

In this study, a field campaign was carried out in a mountainous area of southeastern China during the spring and autumn period. Seasonal concentrations and compositions of ambient VOCs were examined at the county and rural sites, respectively. Moreover, the major VOC sources were quantified using the positive matrix factorization (PMF) model, as well as the chemical reactivity of VOCs to O_3 and SOA formation were discussed. This research could help understand the emissions and environmental impacts of VOCs from small cites in mountainous area and provide a scientific support for policymakers to control local air pollution.

2 METHODS

2.1 Sampling and Analysis

Five sites were selected for the field observation campaign (Fig. 1): Guangze (GZ; 117.33°E, 27.54°N), Jianyang (JY; 118.13°E, 27.33°N), Yanping (YP; 118.17°E, 26.64°N), Pucheng (PC; 118.54°E, 27.92°N), and Tianyou (TY; 117.94°E, 27.65°N), which are located in a mountainous area of southeastern China. GZ, JY, YP, and PC are the county areas of Nanping city, influenced by residential activities, traffic emissions, and industrial processes. TY is located in the Wuyi Mountain Nature Reserve, with less anthropogenic activities and is mainly affected by biogenic VOC emissions. The meteorological conditions and criteria air pollutants during the sampling periods are simultaneously monitored, as shown in Table S1.

VOC sampling were performed in April and September, 2018. A total of 120 ambient air samples at 9:00, 15:00, and 20:00 per day were collected, and each sample was stored in a 3.2 L Silonite™ canister (Entech Instrument, USA). Before VOC sampling, the canisters were cleaned with high-purity nitrogen and then were evacuated to a vacuum. The samples were instantaneously collected, stored at room temperature and were analyzed using a GC/MS system, according to our previous studies (Hu *et al.*, 2018). A total of 100 VOC species were measured, including 28 alkanes, 11 alkenes, 16 aromatics, 34 halocarbons, 10 oxygenated VOCs (OVOCs), and acetylene. The standard gases of TO 15 and PAMS were used to construct the calibration curves for individual VOC. The VOC Standards U.S. EPA PAMS mixture (provided by Spectra Gases Inc., USA) was used in the calibration of PAMS species. Other VOC species were quantified by oxygen standard mixture gas (compendium method TO 15) and then classified in to OVOCs and halocarbons. The targeted VOC species were identified with relative retention time and mass spectra, and were quantified with the internal standard method. The surrogates were added for quality control of sample collection and instrument
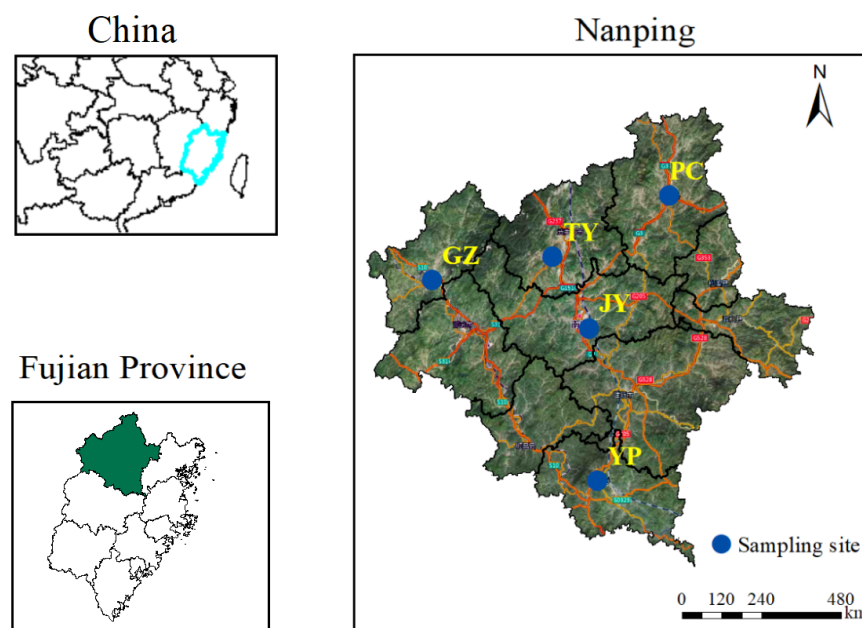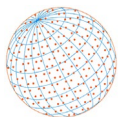
Fig. 1. Locations of the sampling sites in southeast mountain area of China.

analysis. The recovery rate of the surrogates was 96.6 ± 25.0% (April) and 98.4% ± 27.9% (September). The test of the middle point of the standard curve series was repeated for every 12 samples to ensure the accuracy of the data.

2.2 Chemical Reactivity

L_{OH} is usually used to characterize the chemical reactivity of the VOC species, and it is calculated by the following equation.

$$L_{iOH} = [VOC]_i \times K_{iOH} \tag{1}$$

Here, L_{iOH} is the OH radical loss rate of VOC species i, $[VOC]_i$ is the concentration of VOC species i, K_{iOH} is the reaction coefficient of VOC species i with OH radicals, and the K_{iOH} values are from the references (Atkinson *et al.*, 2003; Wilson *et al.*, 2006; Carter *et al.*, 2010).

OFP reflects the maximum potential of VOCs to produce ozone through photochemical reactions. OFP can be estimated using the following equation.

$$OFP_i = [VOC]_i \times MIR_i \tag{2}$$

Here, OFP_i is the ozone formation potential of VOC species i, $[VOC]_i$ is the concentration of VOC species i, and MIR_i is the ozone formation coefficient for VOC species i in the maximum increment reactions of ozone. The MIR_i values are from Carter (1994).

The SOAFP of VOCs was estimated using the following equation.

$$SOAFP_i = [VOC]_i \times FAC_i \tag{3}$$

Here, $SOAFP_i$ is the secondary organic aerosol formation potential (SOAFP) of VOC species i, $[VOC]_i$ is the concentration of VOC species i, and FAC_i is the fractional aerosol coefficient of VOC species i. The FAC_i values are from Grosjean (1992).

2.3 PMF Model

Positive matrix factorization (PMF) is a widely used receptor modelling tool for source analysis. PMF decomposes the receptor matrix (X) into the contribution matrix (G) and profile matrix (F) and then determines the main source and its contribution by the least square method (Tan *et al.*, 2020).
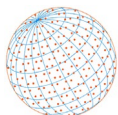
PMF assumes that X is a matrix of data of dimension n rows and m columns. Here, n is the number of samples, and m is the number of species. X can be expressed by matrix G (n × p), F (p × m), and the residual matrix E, where p is the number of factors.

$$X = GF + E \tag{4}$$

The residual matrix E_{ij} can be expressed as:

$$e_{ij} = x_{ij} - \sum_{k=1}^{p} g_{ik} \cdot f_{kj} \tag{5}$$

Here, e_{ij} is the residue factor for species j in sample i, p is the number of pollution sources, x_{ij} is the concentration of species j in the sample i, g_{ik} is the concentration of factor k contribution in sample i, and f_{kj} is the mass percentage of species j in source k.

Factor contribution and profiles are derived by PMF minimizing the objective function Q:

$$Q = \sum_{i=1}^{m} \sum_{j=1}^{n} \left(\frac{e_{ij}}{u_{ij}} \right)^2 \tag{6}$$

Here, u_{ij} is the uncertainty of species j in sample i. u_{ij} is calculated using Eqs. (7) and (8). If u_{ij} is less than MDL, Eq. (7) is adopted. Otherwise, Eq. (8) is adopted.

$$u_{ij} \frac{5}{6} \times MDL \tag{7}$$

$$u_{ij} = \sqrt{(Error\ Fraction \times concerntraion)^2 + (0.5 \times MDL)^2} \tag{8}$$

Here, MDL is the detection limit, and Error Fraction was set to 10% in this study.

2.4 Back Trajectories Analysis

To analyze the air mass origin of different seasons, the TrajStat software was used to calculate backward trajectories (Li et al., 2019; Qin et al., 2021). In this study, 48-hour back trajectories in Nanping (118.18°E, 26.65°N, 500 m above ground level) were calculated with the start height at 500 m altitude and running interval set as every hour a day. The meteorological data used for the analysis were collected from the Global Data Assimilation System (GDAS).

3 RESULTS AND DISCUSSION

3.1 Characteristics of VOCs

Comparisons of different types of VOC species in Nanping and other cities were shown in Table S2. The average concentration of VOCs in the county was 31.9 ppb, and showed the order of OVOCs (11.4 ppb, 35.6% of TVOCs) > alkanes (8.8 ppb, 27.6%) > halocarbons (4.6 ppb, 14.3%) > alkenes (4.0 ppb, 12.4%) > aromatics (2.9 ppb, 9.1%) > alkynes (0.3 ppb, 1.0%). The concentration of TVOCs at the rural site was 22.3 ppb, and exhibited the following order: OVOCs (8.8 ppb, 39.5%), alkanes (5.3 ppb, 23.9%), halocarbons (4.3 ppb, 19.2%), alkenes (2.5 ppb, 11.4%), aromatics (1.1 ppb, 4.8%), alkynes (0.25 ppb, 1.1%). The VOCs concentration in Nanping was significantly lower than those in highly urbanized areas such as Beijing (64.9 ppb) and Shanghai (42.7 ppb), or industrialized city (e.g., Xianghe, 61.0 ppb) in the Beijing-Tianjin-Hebei region (Yang et al., 2019). The VOC concentration at the rural site (22.3 ppb) was similar to that in Guilin (23.7 ppb), a typical tourist city with few industrial emissions (Zhang et al., 2019). In addition, the contribution (35.6%) of OVOCs to TVOCs in Nanping was significantly higher than those in other areas, indicating the dominance of oxidized VOCs in the mountainous area.
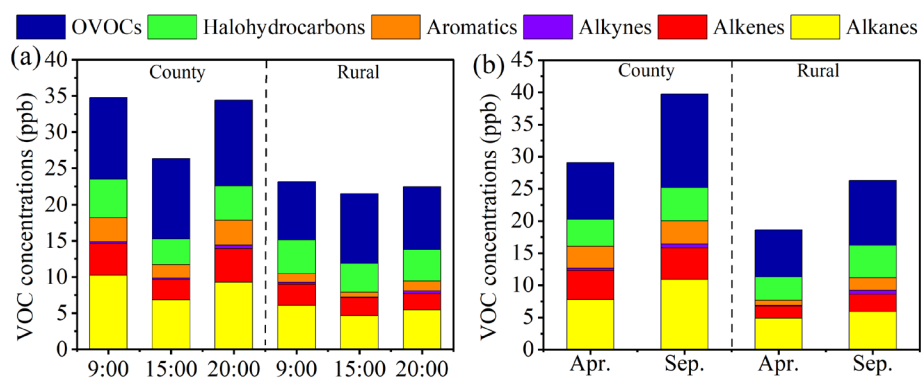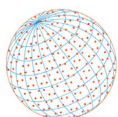
Fig. 2. Temporal variations of VOC concentrations in the county and rural areas.

As shown in Fig. 2, the concentrations of VOCs at the rural site were lower than those in the county, but diurnal variations of VOCs at different sites were similar. At noon with high air temperature and intense solar radiation, the photochemical reaction increased, which leaded to the decrease of VOCs concentrations (Kumar et al., 2018; Hui et al., 2020). In contrast, the low boundary layer height, as well as poor vertical mixing exchange during the morning (9:00) and evening (20:00), might cause the accumulation of VOCs (Kumar et al., 2018). The change of boundary layer height in mountainous areas is more significant than that in urban areas (Helbig et al., 2021). As an important indicator of vehicle exhausts, alkanes showed extremely high concentrations during rush hours (9:00 and 20:00), especially in the county. However, diurnal variations of VOCs at the rural sites was relative constant, except for the influence of boundary layer height.

TVOC concentrations in autumn were significantly higher than those in spring (Fig. 2). The concentrations of OVOCs in September (14.5 ppb in the county areas and 10.1 ppb at the rural site) increased, compared with those in April (8.81 ppb and 7.32 ppb). This was related with temperature and atmospheric oxidized capacity, and the photo-oxidation of VOCs was the main pathway of OVOCs formation during the warm seasons (Gao et al., 2018). Yang et al. (2018) also found that photochemical reactions have a strong influence on the formation of carbonyls, and secondary transformation might have a great contribution to the enhancement of OVOCs.

3.2 Characteristics of Biogenic VOCs

Due to high vegetation coverage, the characteristics of VOCs in Nanping city could be affected by biogenic VOCs. As a typical species of BVOCs, the pattern of isoprene is discussed in this section. The comparison of isoprene in different cities were shown in Table S3. The average concentrations and proportions of isoprene in Nanping (0.25 ppb, 0.91% in the county areas and 0.55 ppb, 2.73% at the rural site) were significantly higher than those in other urban sites such as Shanghai (0.04 ppb, 0.04%) and Beijing (0.07 ppb, 0.01%), but lower than that in Dinghu mountain (0.76 ppb, 3.9%), as a background site in the tropical forest. In this study, the proportion of isoprene was much higher at the rural site than that in the county areas.

As shown in Fig. 3, the temporal pattern of isoprene in the county and the rural site were analyzed. Diurnal and seasonal variations of isoprene proportions to the total VOCs were observed. The largest percentage of isoprene (6.5%) was found at 15:00 and in September, due to the influence of high temperature. This phenomenon was pronounced at the rural site, since isoprene is mainly emitted from plants metabolism, and the emission increases exponentially with ambient temperature (Guenther et al., 1995).

3.3 Chemical Reactivity

Fig. 4 shows the chemical reactivity (L_{OH} and OFP) of different VOC species at the rural and county sites. The contribution of VOC species to the total L_{OH} was the order of alkenes (66.0%), followed by alkanes, aromatics, and OVOCs, accounting for 17.5%, 11.6%, and 4.84%, respectively. Alkenes accounted for 6 and 7 of the top 10 VOC species in the county areas and rural site, respectively (Fig. 4(c)). The results indicated that alkenes played an important role in the chemical
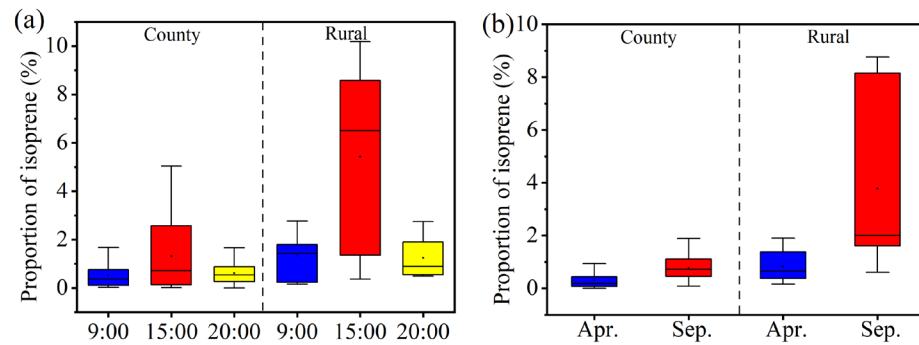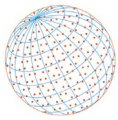
Fig. 3. Box plot for the proportions of isoprene (a) at 9:00, 15:00, and 20:00, (b) in April and September. The whiskers represent the 5–95th percentiles, and the box shows the 25–75th percentiles. The dots indicate the arithmetic average, and the line in the box represents the median.
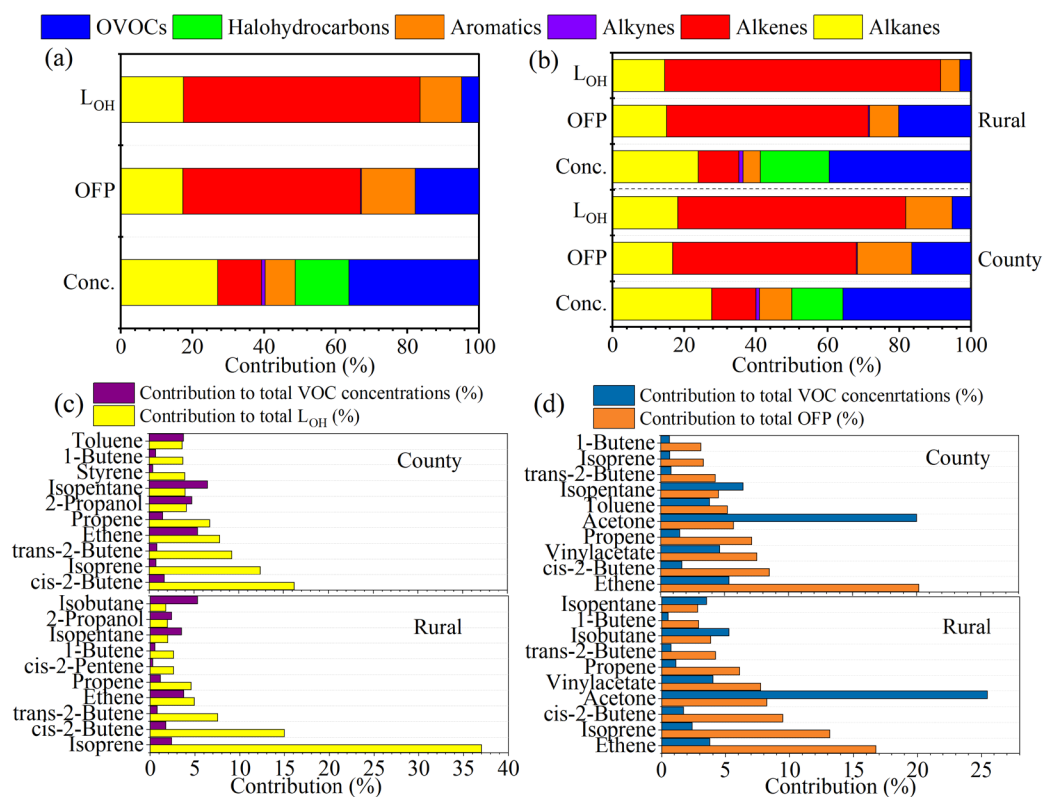

Fig. 4. Chemical reactivity of different VOC species. (a) Contribution of VOC species to total L_{OH}, OFP, and concentration. (b) Contribution of VOC species to L_{OH}, OFP, and concentration in the county areas and rural site. (c) Top 10 VOC species contributing to L_{OH}. (d) Top 10 VOC species contributing to OFP.

reactivity in Nanping, similar to the findings of previous studies (Hui *et al.*, 2018; Mozaffar *et al.*, 2020). High abundance of alkene was normally associated with vehicle exhausts, LPG usage, and biogenic sources (Hui *et al.*, 2020). In this study, the contribution of isoprene to the total L_{OH} at the rural site (37.0%) was significantly higher than that in the county (12.4%). In addition, styrene and toluene contributed a lot to the L_{OH} in the county, which were associated with industrial emissions and solvent use (Hui *et al.*, 2018).

As shown in Fig. 4(d), alkenes contributed most to the total OFP (49.6%), followed by OVOCs, alkanes, and aromatics, accounting for 17.8%, 17.4%, and 14.9%, respectively. The top 10 VOC species contributing the most to OFP were similar to those of L_{OH}. The contribution of alkenes was much higher than that of other VOC species, and ethene contributed most both at the rural
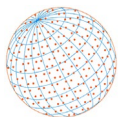
site (16.8%) and county sites (20.2%). In addition, cis-2-butene, trans-2-butene, and propene were also the main components among the top 10 species. Similar to that of L_{OH}, the contribution of isoprene to OFP at the rural site was much higher than that in the county. Differently, OVOCs contributed more to OFP than L_{OH}. Among the 10 VOC species, shown in Fig. 4(d), acetone and vinyl acetate were the representative species for key OVOCs contributed to the OFP. As a key intermediate from the photooxidation of hydrocarbons, acetone was a major source of free radicals and a precursor of ozone and secondary organic aerosol (Chen et al., 2014). Although the concentration of alkanes (27.0%) in Nanping was much higher than that of alkenes (12.0%) and comparable to that of OVOCs (36.3%), the chemical reactivity of alkanes was relatively low. Totally, chemical reactivity (L_{OH} and OFP) of VOC species, especially for isoprene, were obviously different at the rural and county sites.

In the county areas, the total OFP at 15:00 was lower than those at 9:00 and 20:00, and the total OFP in September was higher than that in April (Fig. 5). The results was consisted with the diurnal variations of VOC concentrations. Meanwhile, alkenes were found to be the main contributors to L_{OH} and OFP, followed by alkanes (Fig. 5 and Fig. S1). The total L_{OH} in the county areas was relatively low at 15:00 and in September, and the reversed pattern at the rural site was observed, probably due to the high contribution of alkenes (especially isoprene) to total L_{OH} at the rural site during the warm seasons. In addition, OVOCs played important roles in the total OFP, and showed a more contribution at 15:00 and in September, indicating the influence of photochemical reaction.

Fig. 6 shows the top 10 VOC species contributing to SOAFP. Aromatics accounted for seven VOC species at both rural and county sites. Toluene was ranked as the highest SOAFP value-producing compound, which contributed 43.0% and 27.7% to total SOAFP in the county areas and rural site, respectively. Zhang et al. (2017) and Mozaffar et al. (2020) also mentioned toluene as the main SOAFP species in other Chinese cities. Besides anthropogenic VOCs, BVOCs including isoprene were also important contributors to the formation of SOA. Isoprene was ranked as the 10th and 4th highest SOAFP contributor in the county and rural site, respectively. The results indicated that isoprene cannot be ignored in the SOA formation in inland small city of southeast China.

Fig. S2 shows the distribution of SOAFP at the monitoring sites. The total SOAFP in the county was much higher than that at the rural site, which was attributed to the contribution of aromatics
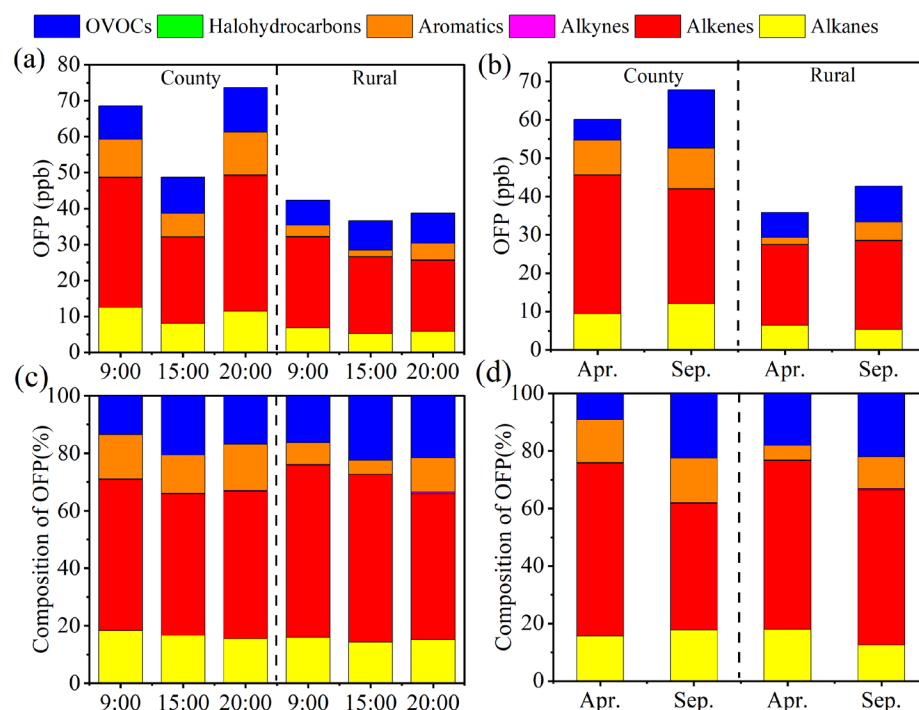

Fig. 5. OFP in the county areas and rural site (a) at 9:00, 15:00, and 20:00, (b) in April and September, Compositions of VOC species to total OFP in the county areas and rural site (c) at 9:00, 15:00, and 20:00, (d) in April and September.
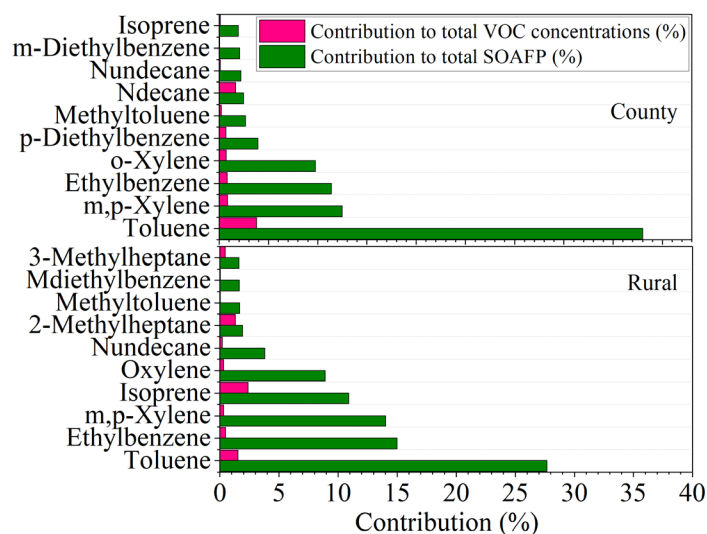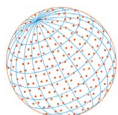
Fig. 6. Top 10 VOC species contributing to SOAFP.

emitted from vehicle exhaust and solvent use. It was reported that aromatics were the dominant SOAFP contributors since they presented higher photo-oxidation rates than other VOC groups (Zheng *et al.*, 2021). In this study, the SOAFP of aromatics was lower at 15:00, suggesting the removal of photochemical reactions and atmospheric diffusion. However, the SOAFP of alkanes showed no obvious diurnal and seasonal variations. At the rural site, isoprene contributed to the total SOAFP was significantly increased, especially at 15:00 and in September. Due to the contribution of isoprene, the total SOAFP at 15:00 was higher than that at 20:00.

3.4 Source Apportionment
3.4.1 Ratio of typical VOC species

Ratios of typical VOC species were frequently used to identify emission sources (Li *et al.*, 2019; Hui *et al.*, 2020). In this study, the ratios of toluene to benzene (T/B), m,p-Xylene to ethylbenzene (X/E), and i-pentane to n-pentane (I/N) were calculated (Table 1). The T/B ratio varied in the range of 1–2 when the atmosphere was mainly impacted by vehicle emissions. Low T/B ratio (< 0.6) indicates strong influences from biomass burning, and industrial activities and solvent usage are more dominant when the T/B ratio is greater than 3 (Li *et al.*, 2019). In this study, the mean ratio of T/B was 4.55 in the county areas, while it was 0.32 at the rural site. The results indicated the mixed impacts from anthropogenic activities including industrial sources and solvent usage in the county areas and the influence of combustion at the rural site.

The ratio of X/E is generally used as an indicator of the photochemical aging of air masses (Kumar *et al.*, 2018). Since m,p-Xylene has a shorter lifetime than ethylbenzene in the air, high X/E ratios indicated fresh air masses, and lower X/E ratios represented aged air masses (Hong *et al.*, 2019; Li *et al.*, 2019). In this study, the mean ratio of X/E at the rural site was lower than that in the county areas (Table 1). The results suggested that anthropogenic VOCs at rural site mainly came from regional transport, and more oxidized air masses were observed. In contrast, primary emissions from local sources majorly contributed to individual VOC species in the county areas. In addition, the ratio of I/N reflects the influence from gasoline evaporation and vehicle emissions (Hong *et al.*, 2019). The mean ratio of I/N in the county areas (3.31) was higher than that at the

Table 1. Ratios of toluene to benzene (T/B), m,p-Xylene to ethylbenzene (X/E), and i-pentane to n-pentane (I/N) in the county areas and rural site.

Ratio	County areas	Rural
T/B	4.55 ± 0.73	0.32 ± 0.35
X/E	1.30 ± 0.03	0.84 ± 0.05
I/N	3.31 ± 0.19	1.74 ± 1.97
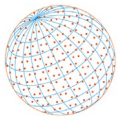
rural site (1.74), indicating the contributions of anthropogenic activities to VOC species in the county areas.

3.4.2 PMF analysis

The PMF model was further used to quantitatively analyze the sources of VOCs in the rural and county areas, as well as the relative contribution of each potential source. As shown in Fig. 7, based on the dominant contribution analysis of typical VOC species, five main sources were identified. Factor 1 was distinguished by a strong presence of isoprene (91.0%), an indicator of biogenic emissions (Wu et al., 2016). Isoprene can also be emitted from industrial production with a large contribution of 2-methylpentane and 3-methylpentane (Li et al., 2015). However, 2-methylpentane and 3-methylpentane contributed little to factor 1, which were 10.8% and 7.52%, respectively. Therefore, factor1 was regarded as biogenic source.

Factor 2 was characterized by high percentage of ethene (66.3%), n-butane (58.1%), isopentane (32.4%), 3-methylpentane (39.5%), propene (51.4%), 1-butene (48.5%), acethlene (50.7%), benzene (37.6%), and toluene (31.1%). These VOC species are usually originated from vehicle exhausts (Heeb et al., 1999; Cai et al., 2010; Liu et al., 2019; Hui et al., 2020). Thus, factor 2 was primarily related to vehicle emissions.

Factor 3 was associated with high loadings of aromatic species, such as ethylbenzene (64.38%), m,p-Xylene (81.4%), styrene (46.2%), o-xylene (72.8%), and toluene (28.5%). Previous studies found that aromatics could be emitted from solvent use or vehicular exhausts. Factor 3 was considered as solvent use, due to the poor correlation among the aromatics and other combustion tracers such as ethene and ethane (Shao et al., 2016).
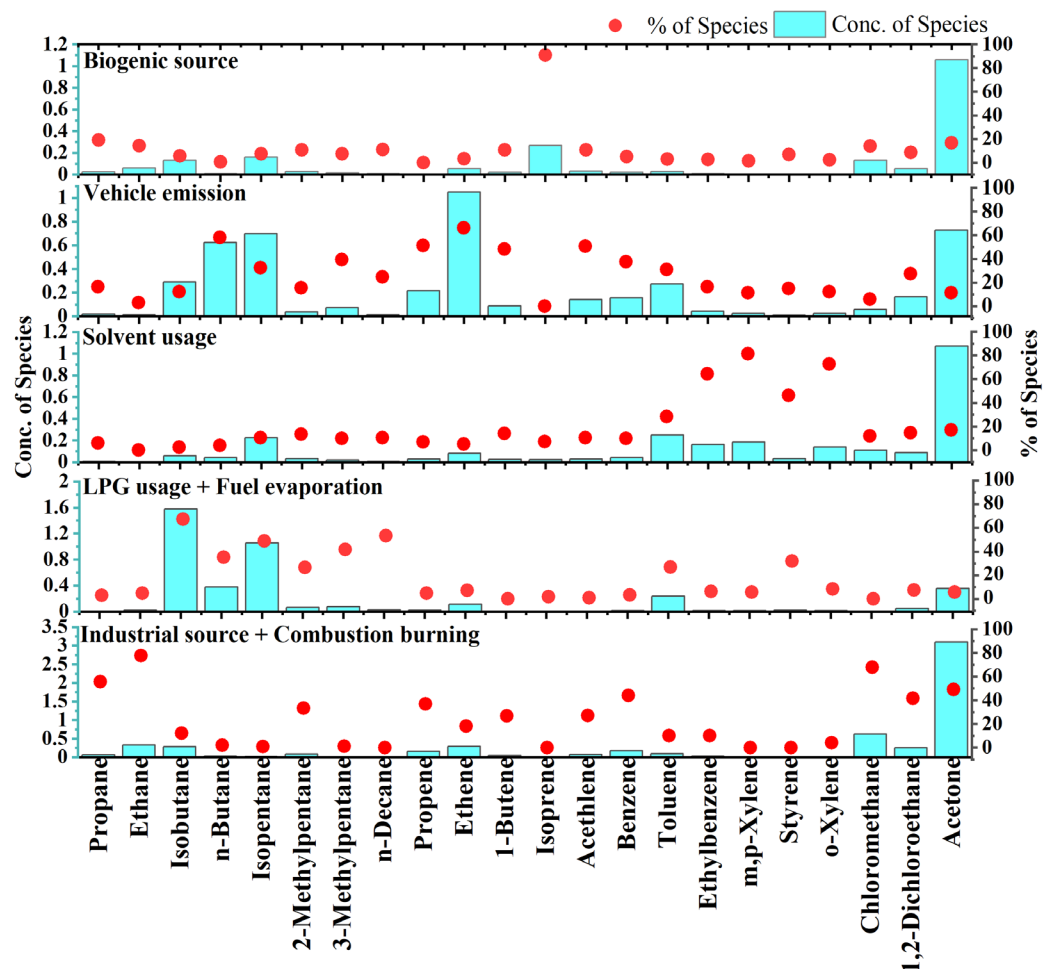

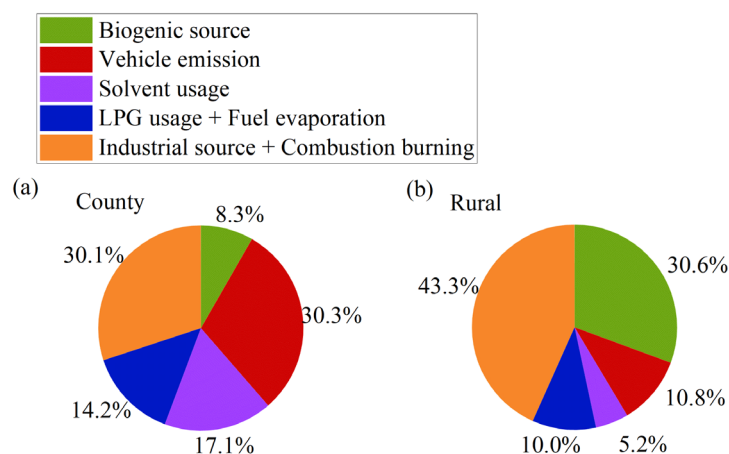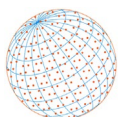**Fig. 7.** Source profiles for the PMF analysis.

Fig. 8. Source apportionment of ambient VOCs in the (a) county and (b) rural site.

Factor 4 had high proportions of C4–C7 alkanes, especially isobutane (67.5%), N-decane (53.5%), isopentane (49.0%), and 3-methylpentane (41.8%), which are mainly associated with gasoline and diesel evaporation (Hui *et al.*, 2020). Isobutane is also a typical tracer for LPG usage (Cai *et al.*, 2010). Thus, factor 4 was identified as LPG usage and fuel evaporation.

Factor 5 was characterized by a significant amount of chloromethane (68.0%), 1,2-dichloroethane (41.7%), acetone (49.2%), and propene (37.0%), which had high contribution from industrial activities (Li *et al.*, 2015; Huang *et al.*, 2019). It was also characterized by an amount of ethane (77.7%) and benzene (43.9%). Ethene, benzene, and chloromethane are tracers associated with combustion sources (Zhang *et al.*, 2021a), and 1,2-dichloroethane is also an important tracer for coal burning (Wu *et al.*, 2016). Therefore, the factor was considered as industrial source and combustion burning.

According to the PMF analysis above, five factors were identified as the main VOC sources in Nanping. Fig. 8 shows the relative contributions of VOC sources to the measured VOCs concentrations in the monitoring sites. The main sources in the county areas included industrial source + combustion burning (30.1%) and vehicle emission (30.3%), followed by solvent usage (17.1%), LPG usage and fuel evaporation (14.2%), and biogenic source (8.31%). At the rural site, although the percentage of industrial source and combustion burning were enhanced, combustion contributed most to the measured VOC concentrations. This is consistent with the results obtained in Section 3.4.1. Biomass burning played an important role in the primary emissions of VOCs in rural areas. Also, biomass boiler was used for rubber and plastic industry distributed sporadically in suburban areas of Nanping city. It was worth noting that biogenic sources at the rural site accounted for 30.6%, which is nearly four times higher than that in the county areas (8.3%). However, the contributions of biogenic sources were found to be less than 10% in urban areas, such as Beijing (2.0%), Nanjing (5.0%), Hong Kong (7.0%), and Pearl River Delta (2.0%) (Zhang *et al.*, 2018). In this study, the contributions of vehicle emission (10.8%), LPG usage and fuel evaporation (10.0%), and solvent usage (5.2%) at the rural site were significantly lower than those (17.1%) in the county areas. Among these sources, the contribution of solvent usage was less than one-third of that in the county areas. The emission from solvent usage (e.g., asphalt paving, architectural coatings, and dry cleaning) is more popular in the county areas. These results could be attributed to high vegetation coverage, low population density, less industrial and commercial activities in Nanping.

3.4.3. Effects of regional transport

As shown in Fig. 9, 48-hour backward air trajectories were calculated using the HYSPLIT model. In April, air masses in Nanping were mainly affected by regional transport from southern cities such as Zhangzhou and Xiamen. However, in September, air masses through the long-range transport were mainly from the north areas, especially the Yangtze River Delta region with large amount of anthropogenic VOCs emissions (Zhang *et al.*, 2018). This was consisted with the results of high TVOCs concentrations in September. Seasonal variations of East Asian Monsoon were happened in the coastal area of Southeast China, which would bring clean air masses from the
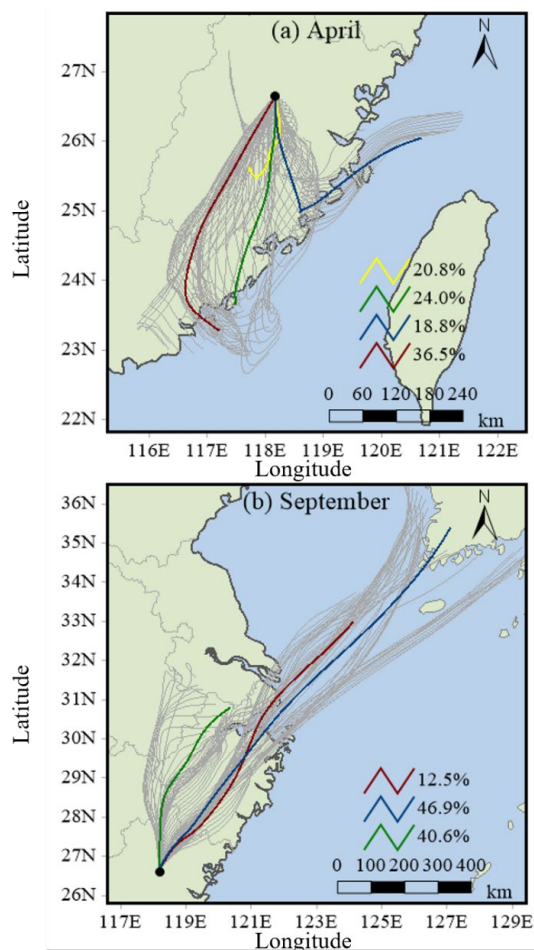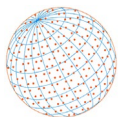
Fig. 9. Cluster analysis of 48 h backward air trajectories and the percentage of each cluster during the sampling periods using the HYSPLIT model.

southern ocean in spring and summer, and polluted air masses from northern continents in autumn and winter (Hong *et al.*, 2019; Wang *et al.*, 2021).

4 CONCLUSIONS

Seasonal variations of ambient VOCs and their contributions to O_3 and SOA in southeast mountainous area of China were investigated. The concentrations of TVOCs in the country areas were significantly lower than those in urban areas of China. Oxygenated VOCs were the main contributors to the formation of O_3 and SOA, indicating the influence of atmospheric oxidation capacity and regional transport. Alkenes presented the strongest chemical activity and accounted for a large proportion of the top 10 species to the total L_{OH} and OFP. As an indicator of biogenic source, isoprene had a greater contribution to O_3 and SOA formation than that in urban areas, due to high vegetation coverage in Nanping. Aromatics were the largest SOAFP contributors at both county and rural areas. The PMF results suggested that ambient VOCs in the county areas were mainly originated from anthropogenic activities, including industrial and combustion burning (30.1%), and vehicle exhausts (30.3%), followed by solvent usage (17.1%), LPG usage and fuel evaporation (14.2%), biogenic source (8.31%). The air mass arriving at the monitoring sites in autumn were mainly from the northern continents with large number of anthropogenic VOCs, which led to high concentrations of VOCs than that in spring. It is worth pointing out that biogenic sources accounted for 30.6% at the rural site had a great contribution to O_3 and SOA formation, which was nearly four times higher than that in other urban areas. This brings difficulties to the control of secondary pollution at rural areas.
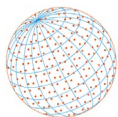
Based on sources apportionment of VOCs, the local governments could take effective control measures to improve air quality. In rural areas, it is necessary to prohibit the activities of biomass burning. As for county areas, we should pay more attentions to avoid the traffic jams and encourage new energy vehicles. Then, the reduction of industrial emissions could be achieved by installing VOC control facilities and replacing oil-based paint with water-based paint. In addition, the emissions control of gas stations, dry cleaners and asphalt paving should be strengthened.

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DISCLAIMER

The authors declare no conflict of interest.

SUPPLEMENTARY MATERIAL

Supplementary material for this article can be found in the online version at https://doi.org/10.4209/aaqr.220016

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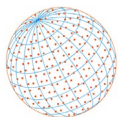
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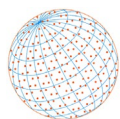
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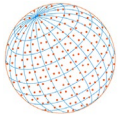
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