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# Emissions of volatile organic compounds (VOCs) from cooking and their speciation: A case study for Shanghai with implications for China

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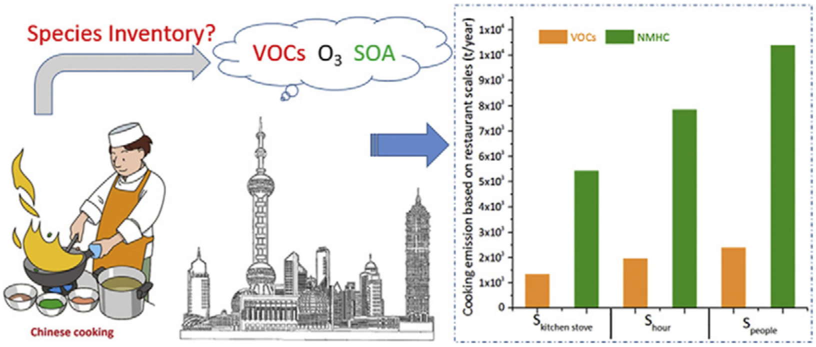
## HIGHLIGHTS

- The VOC compositions of cooking emissions in Shanghai and their chemical reactivity were provided.
- Alkane and oxygenated VOCs (O-VOCs) dominated the VOC emissions.
- Three VOC emission factors (EF) for restaurants emitted VOCs were developed and discussed.
- Two methodologies were defined for deriving VOC emission inventories based on cuisine types and restaurant scales.
- VOC Emissions in other provinces are obtained based on Environmental Kuznets Curve.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Cooking emission is one of sources for ambient volatile organic compounds (VOCs), which is deleterious to air quality, climate and human health. These emissions are especially of great interest in large cities of East and Southeast Asia. We conducted a case study in which VOC emissions from kitchen extraction stacks have been sampled in total 57 times in the Megacity Shanghai. To obtain representative data, we sampled VOC emissions from kitchens, including restaurants of seven common cuisine types, canteens, and family kitchens. VOC species profiles and their chemical reactivities have been determined. The results showed that 51.26% ± 23.87% of alkane and 24.33 ± 11.69% of oxygenated VOCs (O-VOCs) dominate the VOC cooking emissions. Yet, the VOCs with the largest ozone formation potential (OFP) and secondary organic aerosol potential (SOAP) were from the alkene and aromatic categories, accounting for 6.8–97.0% and 73.8–98.0%, respectively. Barbequing has the most potential of harming people's heath due to its significant higher emissions of acetaldehyde, hexanal, and acrolein. Methodologies for calculating VOC emission factors (*EF*) for restaurants that take into account VOCs emitted per person ($EF_{person}$), per kitchen stove ($EF_{kitchen\ stove}$) and per hour ($EF_{hour}$) are developed and discussed. Methodologies for deriving VOC emission inventories (S) from restaurants are further defined and discussed based on two categories: cuisine types ($S_{type}$) and restaurant scales ($S_{scale}$). The range of $S_{type}$ and $S_{scale}$ are 4124.33–

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7818.04 t/year and 1355.11–2402.21 t/year, respectively. We also found that $S_{type}$ and $S_{scale}$ for 100,000 people are 17.07–32.36 t/year and 5.61–9.95 t/year, respectively. Based on Environmental Kuznets Curve, the annual total amount of VOCs emissions from catering industry in different provinces in China was estimated, which was 5680.53 t/year, 6122.43 t/year, and 66,244.59 t/year for Shangdong and Guangdong provinces and whole China, respectively. Large and medium-scaled restaurants should be paid more attention with respect to regulation of VOCs.

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## 1. Introduction

Volatile organic compounds (VOCs), as important precursors of ozone and secondary organic aerosols (SOAs), are critical for the formation of photochemical smog and fine particulate matter in the atmosphere (Atkinson, 2000; Volkamer et al., 2006; Kroll et al., 2006; An et al., 2014). These deleterious compounds have a significant impact with respect to climate change and air quality, and cause adverse health effects in people (Fiore et al., 2008; Wu et al., 2016). The role of VOCs in terms of air quality in China and Southeast Asia has becoming more and more serious, owing to the unsound emission standards and waste disposal measures. Currently, the waste disposal measures were mainly focused on large size particles. And the measures for VOCs was at the initial stage, and VOCs treatment efficiency was about 54% (Deng, 2008). Urban areas among a number of cities in these regions are suffering from haze, and SOAs have been proven to be one major factor (Huang et al., 2014; Guo and Lakshmikantham, 2014). In addition, the problem of ozone pollution is becoming more and more serious in East and Southeast Asia (Wang et al., 2017). There have been already a number of studies on cataloging VOC emission inventories originating from vehicles, biomass burning and industrial processes, especially in China (Bo et al., 2008; Guo et al., 2007; Huang et al., 2011a; Liu et al., 2005; Yin et al., 2015; Zheng et al., 2017). Few studies compare emissions from different cooking processes, but do not characterize how cooking emissions enter into the ambient urban atmosphere (Wang et al., 2017). In China and other countries of Southeast Asia, people often employ high temperature oil (The 'high temperature oil' means the edible oil was heated to a high temperature, about 260 °C) for frying food on a daily basis, resulting other components produced, such as alkanes, which are the dominant contributor in Beijing and Hong Kong (Huang et al., 2011b; Zhang and Ma, 2011). Overall, more than 300 kinds of reaction products have the potential to be released during this cooking process (Wang et al., 2017). One hotspot for air pollution is Eastern China because of its high population density and rapid urbanization.

For this case study, Shanghai was chosen as the largest city in Eastern China. Here, the restaurant business is well developed in terms of both scale and variety. In 2012, the total number (Stats-sh, 2012) of registered restaurants in Shanghai have been 36,692. Characterizing VOC emissions and their reactivity profiles from such a large commercial sector is thus an urgent issue, which has to be investigated and understood. Exploring the species profiles of VOCs produced from cooking in Shanghai's urban area and creating emission inventories will allow for meaningful regulatory policy. Furthermore, as a result of the complexities in the methodologies of quantifying VOC emissions from various cuisine types, and the unexpected randomness of customer preference, the methodologies for building up inventories for VOC emissions arising from urban cooking and quantifying their related emission factors have not been well established yet.

Cooking emissions are generated via intensive chemical reactions occurring with edible oil or food under high temperatures by three major pathways: 1) thermal oxidation and decomposition of the lipid; 2) Maillard reaction of some chemical species; 3) secondary reaction of the intermediates or final products (Zhang and Yang, 2006). VOCs mainly come from heated oils and fatty acids. The former is related to triglycerides, of which the double bond location and the fracture location cause generation of different hydroxyl species and further leads to decomposition into alkanes, alkenes and OVOCs (Choe and Min, 2006).

Motivated by this urgent need, this study represents the initial foray into establishing a VOC emissions inventory that represents multiple residential and commercial kitchens in Shanghai. A total of 57 rounds of in-situ measurements of VOC emissions from the extraction stacks of restaurants for seven cuisine types in Shanghai, including canteens and family kitchens, were investigated. The aim was to identify the similarities and differences between VOC compositions and their chemical reactivity among the different types of urban kitchens, and propose methodologies for deriving VOC emission factors and inventories.

## 2. Materials and methods

All restaurants were compared by employing a classification scheme based on cuisine types and restaurant scales. For each classification, emissions per person, per kitchen stove, and per hour, as well as which emission factors are most recommended, are discussed.

### 2.1. Sampling methodology

Restaurants of seven cuisine types were selected for sampling at their emission extraction stacks, including: authentic Shanghai cuisine, shaoxing cuisine, cantonese cuisine, western fast food, Sichuan and Hunan cuisine, fried food and barbecue. Canteens and family kitchens were also investigated. We have selected representative restaurant for each type. There were 27, 6, 2, 8, 2 and 4 samples for Canteen, Authentic Shanghai Cuisine, Shaoxing Cuisine, Cantonese Cuisine, Western Fast Food, Sichuan and Hunan Cuisine. The sampling time was chosen to be during lunch (11:30–13:30) or dinner (16:30–18:30) periods. Two to three samples were collected continuously for each round of measurement. Detailed information is given in Table SI1.

The sampling point was set at 0.5 m over or from the extraction stack. An airflow rate meter (SC-8000S, China) was used to measure the flow rate in extraction stack, and the air flow was obtained by multiplying the cross-sectional area (circular pipe and rectangular). 3.2 L SUMMA canisters, pipes and connections were cleaned several times with ENTECH equipment before each measurement, and followed with vacuum backup. Each canister was connected with a Teflon filter to remove particulate matter and moisture during sampling. Real-time monitoring of non-methane hydrocarbons (NMHCs) was conducted using a J.U.M 3-900 heated flame ionization detector (FID) total hydrocarbon analyzer. The setup is shown in Figure SI1.

### 2.2. VOCs analysis

The collected samples were analyzed using gas chromatography-mass spectrometry (GC-MS, Agilent, GC model 7820A, MSD model 5977E). Photochemical Assessment Monitoring Stations (PAMs) were adopted to quantitatively determine 99 VOC species. All samples went through the automatic sampler for precooling enrichment treatments prior to entering the GC-MS. The precooling concentrator extracted a certain amount of samples by trapping them into a $^1/_4$ in. liquid nitrogen trap. After the water and $CO_2$ was removed, the samples were separated by GC, and then entered the MS to be spectrometrically analyzed. The temperature program initiated with a 3 min isothermal period at −35 °C, followed by a ramp to 220 °C at a rate of 6 °C/min, and remained at 220 °C for 6 min. The carrier gas was helium. Target compounds were identified using their chromatographic retention times and mass spectra, and the concentrations of target compounds were calculated using internal standard method. The detection limit was from a fraction of μg/m$^3$ to over ten μg/m$^3$ (Agilent, 2012). A commercial standard gas (Spectra, USA) containing PAMS (Photochemical Assessment Monitoring System), O-VOC, and chlorinated volatile organic compounds(x-VOC) was used to identify compounds and confirm their retention times. 99 species including 29 alkanes, 11 alkenes, 16 aromatics, 14 O-VOC, 28 x-VOC and acetylene were identified in this study.

### 2.3. Ozone formation potential

OFP was calculated by taking into account VOC source profiles and the maximum incremental reactivity (MIR) of each species (Carter, 1994), as described by Eq. (1)

$$OFP_i = MIR_i \times VOC_i \tag{1}$$

where $OFP_i$ and $VOC_i$ represents the OFP and concentration of the i$^{th}$ VOCs species (μg/m$^3$). $MIR_i$ is the maximum incremental reactivity of the i$^{th}$ VOCs species (grams $O_3$ per gram VOCs).

### 2.4. Emission factors

Emission factors of VOCs and NMHCs related to per person ($EF_{person}$,g/person), per kitchen stove ($EF_{kitchen\ stove}$, g/h·stove), and per hour ($EF_{hour}$, g/h) were investigated. Background VOC concentrations for each individual measurement were subtracted prior to performing the calculations. Emission factors for VOCs and NMHCs were calculated according to Eqs. (2–4), respectively:

$$EF_{person} = \frac{\sum_i VOC_i \times F \times 10^{-6}}{P} \text{ or } EF_{person} = \frac{NMHC \times F \times 10^{-6}}{P} \tag{2}$$

$$EF_{kitchen\ stove} = \frac{\sum_i VOC_i \times F \times 10^{-6}}{N} \text{ or } EF_{kitchen\ stove} = \frac{NMHC \times F \times 10^{-6}}{N} \tag{3}$$

$$EF_{hour} = \sum_i VOC_i \times F \times 10^{-6} \text{ or } EF_{hour} = NMHC \times F \times 10^{-6} \tag{4}$$

where $VOC_i$ is the mass concentration of species i, μg/m$^3$. $NMHC$ is the mass concentration of NMHC, μg/m$^3$. $F$ is the flow rate, m$^3$/h. $P$ is the hourly number of customers, person/h. $N$ is the number of kitchen stoves in each restaurant.

### 2.5. VOC emissions based on cuisine types

Two categories of emission inventories were included that took into account cuisine types and restaurant scales. $S_{type}$ and $S_{scale}$ represent VOCs emission based on cuisine types and restaurant scales, respectively. According to the previously defined three types of emission factors,

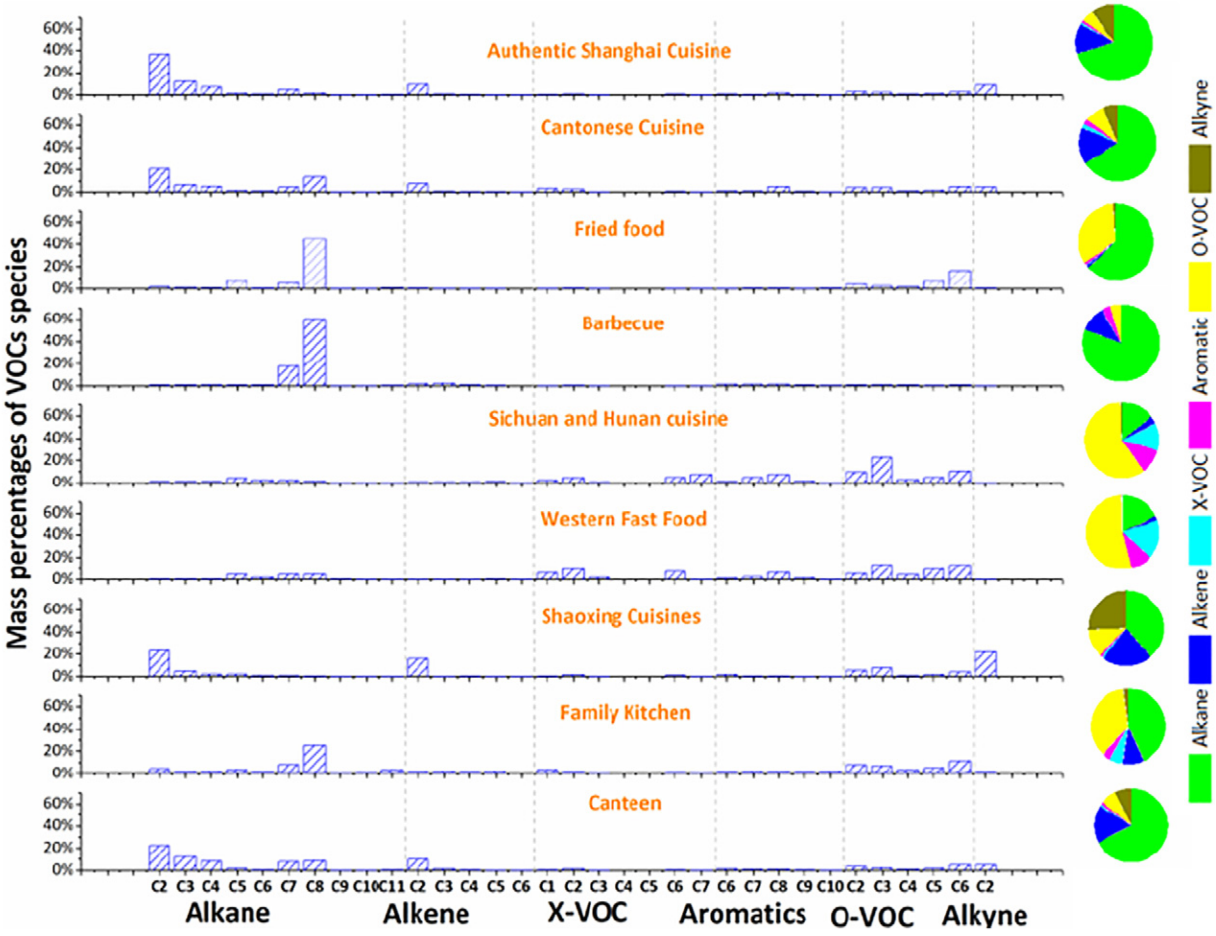

**Fig. 1.** Mass percentages of VOC species according to carbon numbers for each cuisine type.

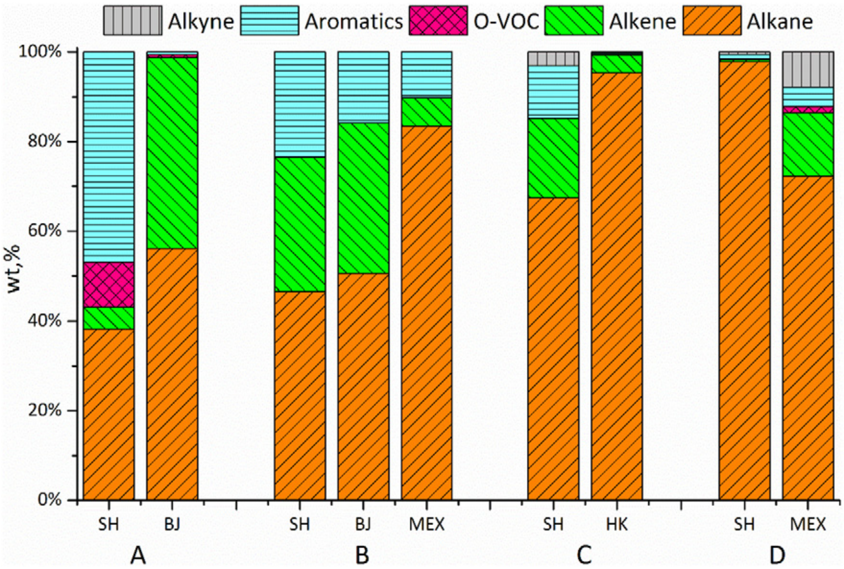

**Fig. 2.** Comparison of compositions of VOCs emitted from different types of kitchens among different studies (A: Sichuan and Hunan cuisine; B: barbecue; C: family kitchen; D: fried food. SH: Shanghai-this study; BJ: Beijing-Zhang and Ma, 2011; HK: Hongkong-Huang et al., 2011b; MEX: Mexico-Mugica et al., 2001.

the first methodology based on $EF_{person}$ was calculated as Eq. (5):

$$S_{person-type} = 52 \times \sum_{j}\left(\sum_{i}(Q \times y_i \times e) \times x_j \times EF_{person\ i}\right) + 52 \times \sum_{t}^{2}\left(\left(Q \times 21 - \sum_{j}\left(\sum_{i}(Q \times y_i \times e \times x_j)\right)\right) \times z_t \times EF_{person\ t}\right) \quad (5)$$

where $Q$ is the population of Shanghai, which was 24,152,700 by the end of 2015 (Stats-sh, 2016); $y_i$ is the percentage of the Shanghai population dining in each restaurant type, %; $e$ is the number of meals per week in restaurants for Shanghai residents; $z_t$ is the percentage of dining frequency taking place in a canteen or at home; $x_j$ is the percentage of customer preferences by cuisine type, %.

The second methodology which is based on $EF_{kitchen\ stove}$ is described by Eq. (6):

$$S_{kitchen\ stove-type} = 365 \times \sum_{i}(EF_{kitchen\ stove} \times T \times Na \times a) + EF_{kitchen\ stove} \times Nc \times t \times 365 \quad (6)$$

where $Na$ is the registered number of restaurants for each cuisine type in Shanghai; $a$ is the number of kitchen stoves for each cuisine type; $Nc$ is the number of families in Shanghai.

The third methodology based on $EF_{hour}$ was calculated from Eq. (7):

$$S_{hour-type} = 365 \times \sum_{i}(EF_{hour} \times T \times Na) \quad (7)$$

where $Na$ is the number of restaurants for each cuisine type; $T$ is the working time of the restaurant kitchens, 4 h.

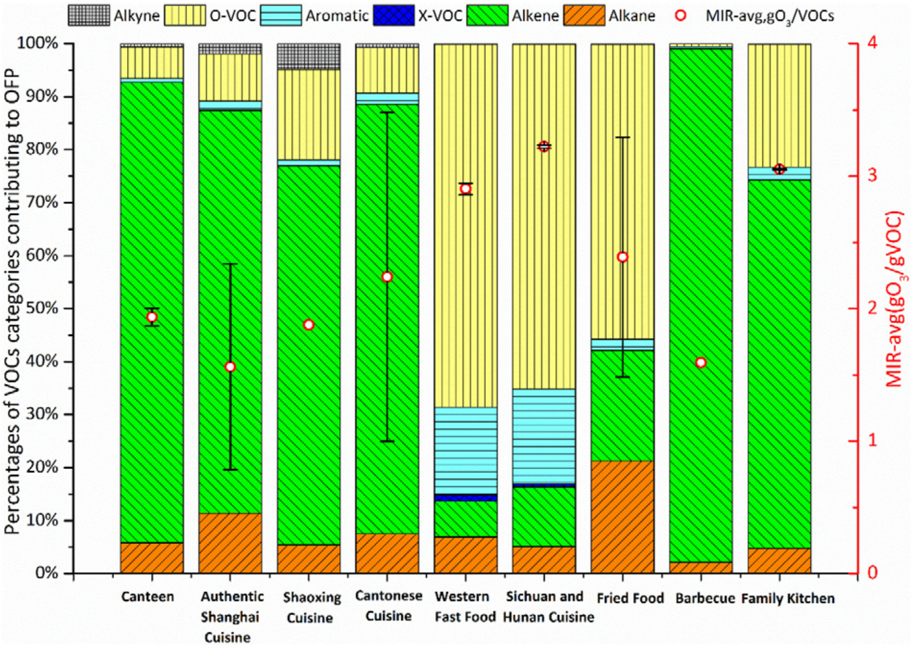

**Fig. 3.** Percentages of VOC categories contributing to OFP and the average MIR for each cuisine type.

**Table 1**
Emission factors based on cuisine types.

| Cuisine (number of samples) | $EF_{people\text{-}type}$ (g/person) VOCs | $EF_{people\text{-}type}$ (g/person) NMHC (by carbon) | $EF_{kitchen\ stove\text{-}type}$ (g/h·stove) VOCs | $EF_{kitchen\ stove\text{-}type}$ (g/h·stove) NMHC (by carbon) | $EF_{hour\text{-}type}$ (g/h) VOCs | $EF_{hour\text{-}type}$ (g/h) NMHC (by carbon) |
|---|---|---|---|---|---|---|
| Canteen (27) | 0.01 ± 0.00 | 0.10 ± 0.03 | 1.97 ± 1.33 | 16.18 ± 10.96 | 15.76 ± 5.94 | 129.40 ± 0.033 |
| Authentic Shanghai cuisine(6) | 2.54 ± 1.30 | 15.55 ± 7.96 | 9.09 ± 2.49 | 55.54 ± 15.22 | 111.04 ± 30.43 | 634.56 ± 7.96 |
| Shaoxing cuisine(2) | 2.26 ± 0.00 | 13.22 ± 0.00 | 12.52 ± 0.00 | 61.33 ± 0.00 | 225.59 ± 0.00 | 1030.22 ± 0.00 |
| Cantonese cuisine(8) | 1.96 ± 1.24 | 8.41 ± 5.30 | 12.04 ± 7.14 | 55.46 ± 32.89 | 78.41 ± 38.66 | 358.54 ± 176.77 |
| Western fast food(2) | 0.32 ± 0.04 | 0.60 ± 0.08 | 1.86 ± 0.24 | 3.47 ± 0.48 | 11.15 ± 1.44 | 20.84 ± 2.69 |
| Sichuan and Hunan cuisine(4) | 0.17 ± 0.00 | 0.25 ± 0.00 | 5.94 ± 0.03 | 8.18 ± 0.04 | 17.80 ± 0.09 | 24.53 ± 0.13 |
| Family kitchen(7) | 0.00 ± 0.00 | 0.02 ± 0.01 | 0.02 ± 0.01 | 0.33 ± 0.07 | 0.12 ± 0.03 | 0.22 ± 0.02 |

### 2.6. VOC emission based on restaurant scales

Three methodologies associated with customers, kitchen stoves and cuisine types are given as Eqs. (8)–(10), respectively.

$$S_{person-scale} = Q \times Nc \times EF_{person} \tag{8}$$

$$S_{kitchen\ stove-scale} = \sum N \times a \times T \times EF_{kitchen\ stove} \times 365 \tag{9}$$

$$S_{hour-scale} = \sum N \times T \times EF_{restruant} \times 365 \tag{10}$$

where $S$ is the total annual emission, t; $Q$ is the Shanghai population; $Nc$ is the customer dining frequency, and according to the aforementioned distribution of the percentage of the Shanghai population dining in restaurants per week, about an value of 100 times/year was obtained for Shanghai people eating in a restaurant(FDA, 2011). $N$ is the number of restaurants for each scale; a is the number of kitchen stoves; T is the working time, 4 h. Snacks and drinks/coffee/tea/bars were classified as small scale restaurants.

## 3. Results and discussions

### 3.1. Speciation of VOCs arising from cooking emissions

The profiles of 99 VOC species were obtained, as listed in Table SI2. The background VOCs concentration has been monitored prior to the measurement in each restaurant and deducted from the sampling. The value accounted very low proportion of total emissions.

Fig. 1 reveals that alkanes were the major VOC pollutant, a fact which can be attributed to the large consumption of peanut oil in Shanghai (He et al., 2013). 51.26% ± 23.87% of alkane and 24.33 ± 11.69% of O-VOCs dominated the VOC cooking emissions. Incomplete combustion of fats derived from meats is a secondary explanation (Hildemann et al., 1991; Rogge et al., 1991). Fugitive emissions from liquefied petroleum gas (LPG) and natural gas (NG), which are usually used as the fuel source for cooking, was another added source of alkanes, leading to the increased prevalence of propane (C3), n-butane (C4), and i-butane (C4). Aldehydes, generated by shallow frying of food, also dominated as a result of the decomposition of fatty acids instead of heated oil (Elmore et al., 1999), and were also major species in most cuisine types.

The investigated cuisine types can be classified into six categories. *1*) *Canteen*, *Authentic Shanghai cuisine and Cantonese cuisine*. The proportion of alkanes was the largest, followed by alkenes and O-VOCs. The main components of the alkanes were ethane (C2) and propane (C3) for canteen and Authentic Shanghai cuisines. C2, C3 and C6 alkanes were the greatest contributors with respect to Cantonese cuisines. *2*) *Shaoxing cuisine*. C2 to C5 alkanes were the largest contributors. Acetylene (C2) dominated as well. A greater quantity concentration of alkenes and O-VOCs were observed, which was possibly due to the use of rice wine and fresh ingredients adopted for stews. The abnormally high acetylene (C2) concentration might be a consequence of the equipment of the facilities. *3*) *Western fast food*, *Sichuan and Hunan cuisine*. C2 ~ C6 alkanes were the major O-VOC contributors for each restaurant type, respectively. Acrolein (C3), n-Hexanal (C6) and acetone (C3) were the dominant contributors. Acrolein (C3) is generated from edible oils and coal burning can emit acrolein (Gaeggeler et al., 2008; Schauer et al., 2001), hence the enhanced consumption of oil is likely to be the reason for the relatively greater O-VOC production. An abundance of acetone (C3) usually exists in vegetables and volatilizes during boiling. One such example are onions (Huang et al., 2011b), which are used very often for these two cuisine types, and are likely a major source for acetone. Evaporative loss of impurities in fuels is a reason for the significant increase of aromatic and X-VOCs (Huang et al., 2011b). *4*) *Fried food*. Alkanes and O-VOCs contributed to over 97% of the total VOCs, owing to meat-derived fats and large quantities of oil, respectively. The dominant species of alkanes were 2, 2, 4-trimethylpentane (C8) and n-pentane (C5). The main components of O-VOCs were n-Hexanal (C6), n-pentanal (C5) and acetaldehyde (C2). *5*) *Barbecue*. Alkanes contributed here over 83%, as a result of the consumption of large amounts of fat and the adoption of charcoal as a fuel. The main alkane compounds were 2, 2, 4-trimethylpentane (C8) and 2-methylhexane (C7). *6*) *Family kitchen*. Alkanes and O-VOCs were 44.7 ± 1.5% and 32 ± 0.6%, respectively. 2,2,4-trimethylpentane (C8) and 2-methylhexane (C7) accounted for the largest percentage for the alkanes. n-Hexanal (C6), acetaldehyde (C2) and acetone (C3) were the main substances of the O-VOCs.

Fig. 2 compares VOC compositions obtained from this study with other studies. Generally, similar results were obtained among all of the different studies, and alkanes were the dominant contributor for all reports. The observed discrepancies can be attributed to differences

**Table 2**
Emission factors based on restaurant scales.

| Scale (number of samples) | $EF_{people\text{-}scale}$ (g/person) VOCs | $EF_{people\text{-}scale}$ (g/person) NMHC (by carbon) | $EF_{kitchen\ stove\text{-}scale}$ (g/h·stove) VOCs | $EF_{kitchen\ stove\text{-}scale}$ (g/h·stove) NMHC (by carbon) | $EF_{hour\text{-}scale}$ (g/h) VOCs | $EF_{hour\text{-}scale}$ (g/h) NMHC (by carbon) |
|---|---|---|---|---|---|---|
| Canteen (27) | 0.01 ± 0.00 | 0.10 ± 0.03 | 1.97 ± 1.33 | 16.18 ± 10.96 | 15.76 ± 5.94 | 129.40 ± 48.80 |
| Extra-large (4) | 1.77 ± 0.32 | 5.72 ± 1.02 | 8.57 ± 1.49 | 40.84 ± 7.11 | 128.94 ± 22.88 | 285.85 ± 50.71 |
| Large (6) | 3.81 ± 0.76 | 19.67 ± 3.95 | 13.56 ± 2.73 | 70.23 ± 14.11 | 189.78 ± 38.14 | 983.26 ± 197.61 |
| Medium (6) | 1.97 ± 0.26 | 8.41 ± 1.10 | 12.03 ± 3.53 | 55.46 ± 16.25 | 78.41 ± 22.98 | 358.53 ± 105.06 |
| Small (4) | 0.18 ± 0.00 | 0.25 ± 0.00 | 5.94 ± 0.03 | 8.18 ± 0.04 | 17.82 ± 0.09 | 24.53 ± 0.13 |
| Fast food (2) | 0.32 ± 0.04 | 0.60 ± 0.08 | 1.86 ± 0.24 | 3.47 ± 0.45 | 11.15 ± 1.44 | 20.84 ± 2.69 |

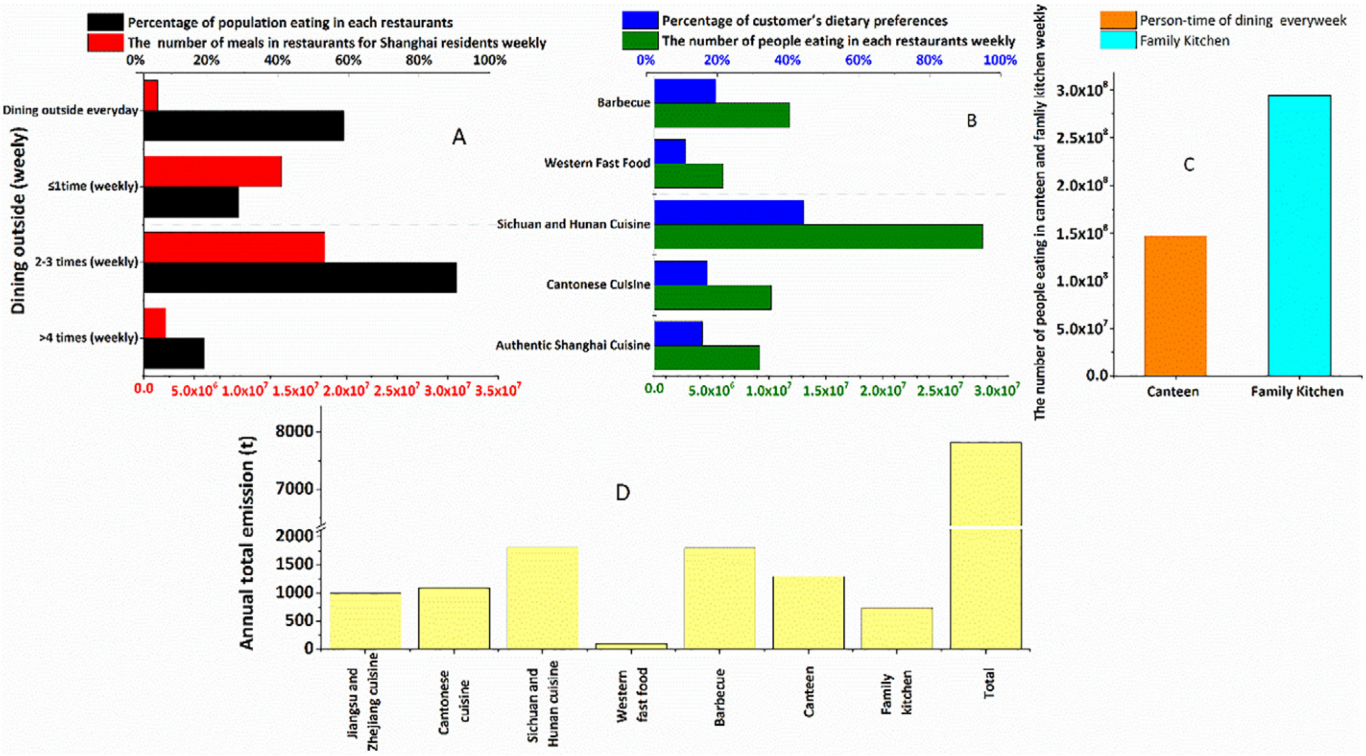

**Fig. 4.** (A) Proportion and the number of people dining frequency for a week. (B) Proportion and the number of people eating in restaurants for each cuisines type. (C) Number of people eating in canteens and household kitchen, respectively. (D) VOCs emission of each cuisine type and the total annual VOCs emissions in Shanghai.

in restaurant scales. Regional differences may lead to different cuisines and food culture.

### 3.2. Ozone formation potential of VOCs

Percentages of OFP for each category of VOCs for all cuisine types are shown in Fig. 3. The average MIR for VOCs from different cuisine types was calculated as the ratio of total OFP to VOC concentration, which can be thought of as the average OFP per unit mass of VOC emission, as given in Fig. 3.

Fig. 3 reveals that the top three contributors to OFP were alkenes, O-VOCs and alkanes for Canteen, Authentic Shanghai cuisine, Shaoxing cuisine and Cantonese cuisine. The chemical reactivity of ethylene and acetaldehyde accounted for 46.9 ± 3.2–69.2 ± 12.5% and 8.0 ± 1.4–11.7 ± 3.5%, respectively. The largest contributors were O-VOCs and aromatics for Western fast food, Sichuan and Hunan cuisine. Acetaldehyde and hexanal accounted for 20.5 ± 1.1–35.2 ± 2.9% and 11.4 ± 2.3–24.1 ± 9.4% of the total OFP, respectively. With respect to barbeque, alkenes contributed to 96.0 ± 12.5% of total OFP. The major contributing species were acrylic acid (25.6 ± 4.6%), isooctane (25.6 ± 4.9%) and

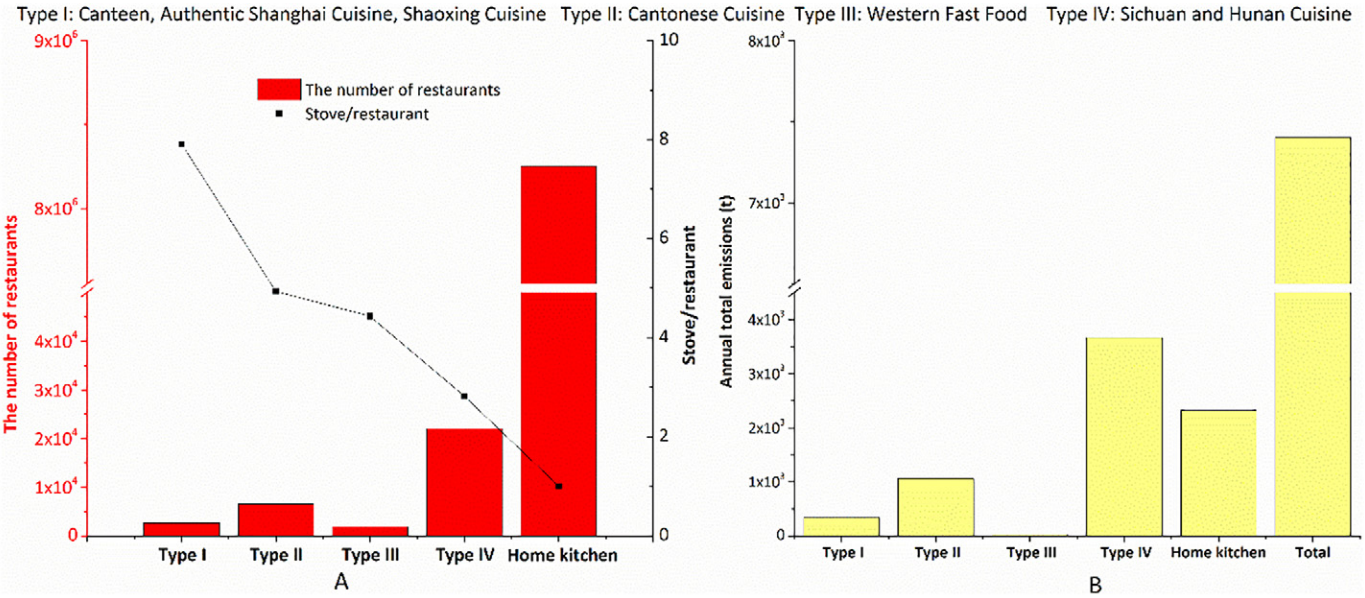

**Fig. 5.** (A) Number of each cuisine type and the corresponding number of kitchen stoves. (B) Annual total VOCs emissions of each type and the total VOCs emissions in Shanghai based on kitchen stove.

**Table 3**
Parameters and emissions with respect to restaurants of various scales.

| Scales | N | a | $S_{\text{kitchen-stove-scale}}$ (t/year) | | $S_{\text{hour-scale}}$ (t/year) | | $S_{\text{people-scale}}$(t/year) | |
|---|---|---|---|---|---|---|---|---|
| | | | VOCs | NMHC | VOCs | NMHC | VOCs | NMHC |
| Canteen | 208 | 2.93 | 1.77 ± 0.12 | 14.44 ± 4.22 | 4.80 ± 1.23 | 39.40 ± 4.56 | – | – |
| Extra large | 100 | 22.25 | 27.92 ± 3.24 | 133.03 ± 34.52 | 18.89 ± 2.33 | 41.86 ± 6.73 | – | – |
| Large | 2392 | 8.54 | 405.53 ± 24.57 | 2100.31 ± 134.56 | 664.60 ± 56.34 | 3443.25 ± 456.22 | – | – |
| Medium | 6590 | 4.93 | 572.19 ± 33.11 | 2637.88 ± 245.67 | 756.52 ± 45.67 | 3459.04 ± 243.20 | – | – |
| Small | 7842 | 2.97 | 202.54 ± 12.59 | 278.92 ± 4.56 | 204.57 ± 19.79 | 281.59 ± 15.34 | – | – |
| Fast food | 1843 | 4.43 | 22.23 ± 5.13 | 41.49 ± 2.47 | 30.08 ± 4.56 | 56.22 ± 7.54 | – | – |
| Snacks | 14,183 | 2.69 | 103.50 ± 7.08 | 193.10 ± 34.23 | 231.50 ± 12.58 | 432.64 ± 45.80 | – | – |
| Drinks/coffee/tea/bar | 3534 | 2.02 | 19.44 ± 2.33 | 36.27 ± 3.56 | 57.69 ± 6.98 | 107.80 ± 7.57 | – | – |
| Total | 36,692 | – | 1355.11 ± 107.24 | 5435.42 ± 185.45 | 1968.61 ± 98.57 | 7861.79 ± 267.56 | 2402.21 ± 145.67 | 10,396.77 ± 345.79 |

ethylene (19.0 ± 7.3%). O-VOCs were the main source of chemical reactivity for Fried food, and isooctane was the largest contributor in alkanes. O-VOCs and alkenes contributed 23.1 ± 3.4% and 69.5 ± 12.6% to the total OFP for family kitchens, respectively. Acetaldehyde (24.2 ± 3.5%), n-hexanal (10.9 ± 4.8%), propylene (10.0 ± 2.7%) and ethane (9.3 ± 3.5%) were the largest contributors. It was also concluded by the data shown in Fig. 3 that the average MIR of VOCs from cooking emissions ranged from $3.0 \times 10^{-12}$ $\text{cm}^3 \cdot \text{molecule}^{-1}\ \text{s}^{-1}$ to $11.5 \times 10^{--12}$ $\text{cm}^3 \cdot \text{molecule}^{-1}\ \text{s}^{-1}$, among which, Western fast food, Sichuan and Hunan cuisine, and family kitchens showed the highest MIR.

### 3.3. SOA formation potential of VOCs

SOA formation potential (SOAP) represents the propensity for an organic compound to form secondary organic aerosols, when that compound is emitted to the ambient atmosphere (Derwent et al., 2010). The value is generally reported relative to the secondary organic aerosol formations of toluene, when an identical mass concentration of the species of interest is emitted into the atmosphere (Derwent et al., 2010; Johnson et al., 2006; Kleindienst et al., 2007; Hu et al., 2008), as described by Eq. (11):

$$SOAP_i = \frac{Increment\ in\ SOA\ mass\ concentration\ with\ species_i\ i}{Increment\ in\ SOA\ with\ toluene} \times 100 \quad (11)$$

SOAP mass-weighted contributions (Derwent et al., 2010) of each VOC category is shown in FigureSI2. Aromatics accounted for 75.34 ± 15.35–98.14 ± 19.54% of the total. The largest contributor was toluene. Although VOCs with low carbon numbers dominated, their contribution to SOA formation can be neglected. The saturated vapor pressures for oxidizing VOCs with low carbon numbers are too high, such that these VOCs do not tend to condense into aerosol phases (Derwent et al., 2010).

### 3.4. VOC emission factors

Based on the information of the number of people and kitchen stoves collected during sampling (Table SI3), the calculated three types of emission factors for each cuisine type are given in Table 1.

According to the Shanghai Municipal Food and Drug Administration, restaurants can be classified into extra-large, large, medium or small scales based on the amount of area occupied and the number of seats (FDA, 2011). Emission factors derived by considering restaurant scales are given in Table 2. Emission factors for both large and medium-sized restaurants were the most significant, and so these restaurant sizes should be the focus for management control.

The variances in Table 2 were generally less than in Table 1, especially for authentic Shanghai and Cantonese cuisines, which taken together accounted for the major portion of large and medium scale restaurants. This result indicates that pollutant emissions entering the ambient atmosphere are mainly determined by restaurant scales. Hence, emission factors based on restaurant scales are recommended for estimating VOCs produced from urban cooking activity. Furthermore, with respect to the emission factors of per person, per kitchen stove and per hour,

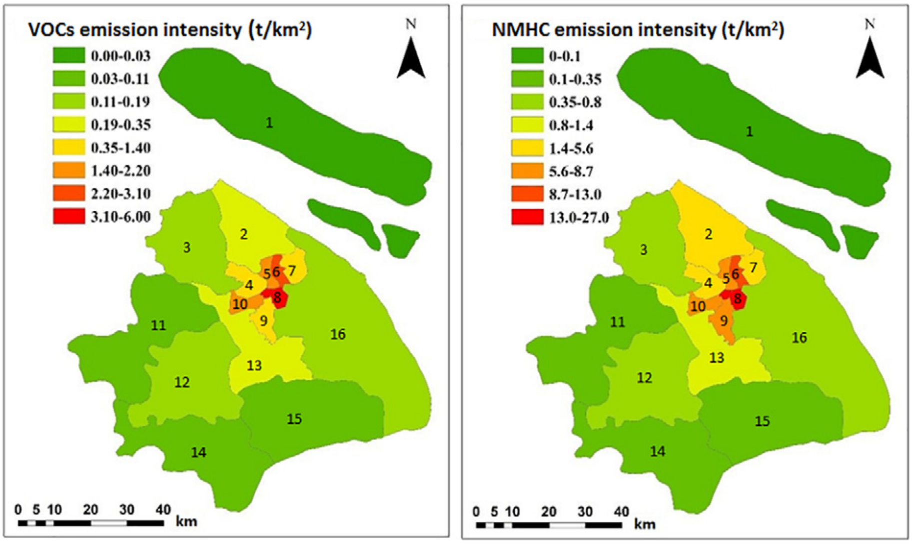

**Fig. 6.** Geographical distributions of the intensities of VOC and NMHC emission from restaurant scales in Shanghai produced by cooking (1.Chongming 2.Baoshan 3.Jiading 4.Putuo 5. Jing'an 6. Hongkou 7.Yangpu 8.Huangpu 9.Xuhui 10.Changning 11.Qingpu 12.Songjiang 13.Minhang 14.Jinshan 15.Fengxian 16.Pudong).

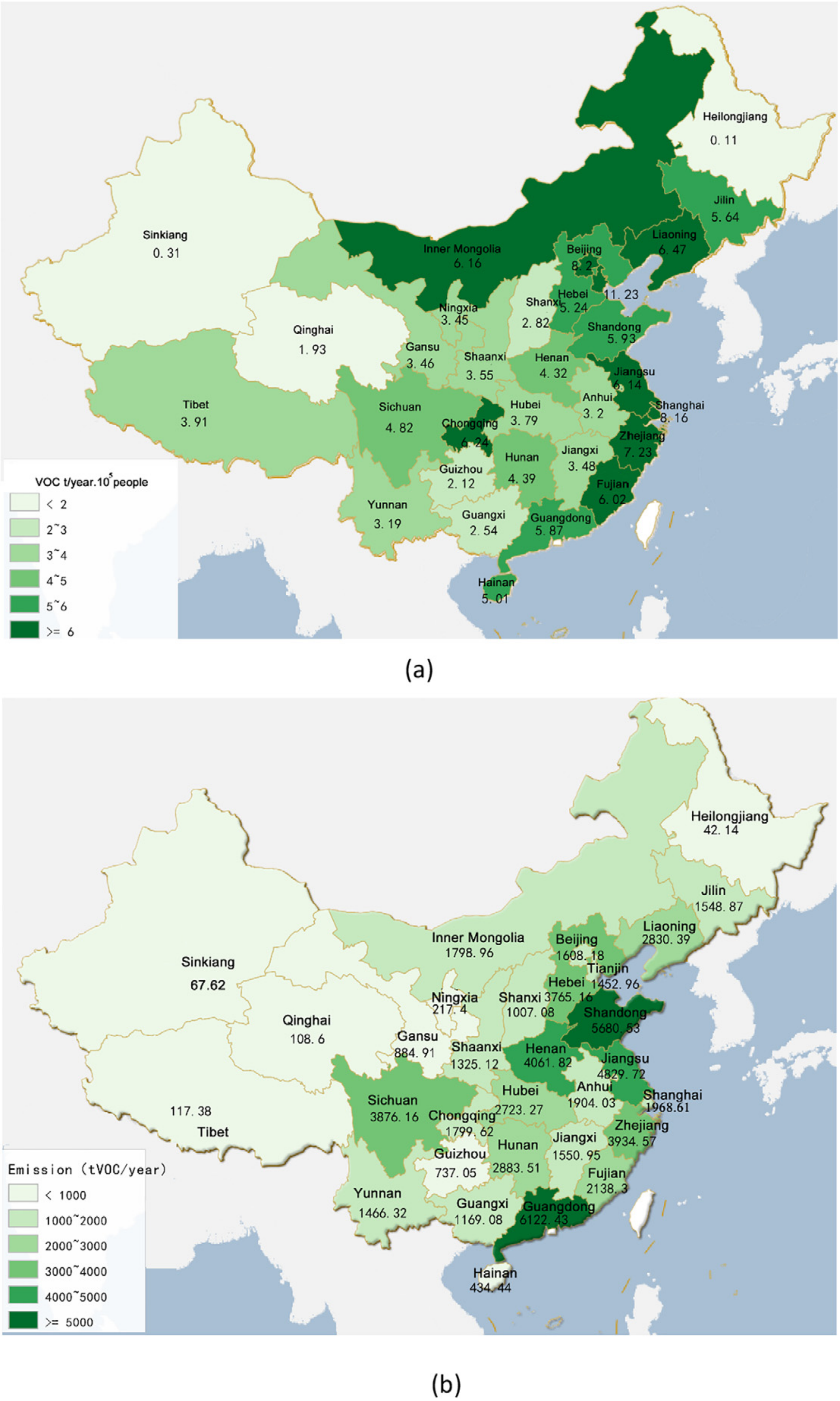

**Fig. 7.** (A) Geographical distributions of the yearly VOCs emissions from restaurant scales of 100,000 people in different provinces. (B) Geographical distributions of the yearly VOCs emissions from restaurant scales of each province in China.

whether all kitchen stoves were turned on and whether the kitchens sampled in the study are enough to provide an accurate representation of the entire population are questions, which still need to be addressed. Therefore, $EF_{hour}$ is recommended as long as the statistical data of the restaurants and the emission concentrations monitored from the extraction stacks of each restaurant is accurate.

### 3.5. VOC emission inventories based on cuisine types

According to a survey conducted by the Chinese Cuisine Association for people dining in restaurants, among all the respondents, 6.2% dined four times a week, 51.1% dined 2–3 times a week, 38.8% dined once or less per week, and 3.9% dined every single day (CCA, 2015), as shown in Fig. 4(A). Then we obtained the Shanghai population dining distributions based on customer dietary preferences (CCA, 2015), as given by Fig. 4(B) and (C). 'Jiangsu and Zhejiang cuisine' is in the official investigation of the dietary data, the Authentic Shanghai Cuisine and Shaoxing cuisine belong to this classification. We assumed a third of the remaining population dine in canteens, and two-thirds eat at home. According to Eq. (5), $S_{person-type}$ of VOC from cooking in Shanghai of 7818.04 ± 254.32 t $Yr^{-1}$ was obtained, as shown in Fig. 4(D). The annual NMHC was found to be 15,226.85 ± 3755.12 t $Yr^{-1}$.

Household emission statistics and the sixth national census showed that the number of households in Shanghai in 2010 was 8.2533 million (SMSB, 2012). The variable $t$ is the working time, which was 4 h. The number of kitchen stoves in Shanghai is given as depicted in Fig. 5(A). Calculated from Eq. (6), we determined the $S_{kitchen\ stove-type}$ of VOC from cooking in Shanghai to be 7403.21 ± 314.29 t $Yr^{-1}$, as shown in Fig. 5(B). The annual NMHC was found to be 11,215.53 ± 1074.36 t $Yr^{-1}$.

The number of registered restaurants in Shanghai in 2012 was 36,692 and can be divided into five categories: canteen/super-huge/large types accounted for 7.4%; the percentage of medium and fast food restaurants was 18.0% and 5.0%, respectively; small scale and snack restaurants contributed to 60.0%; and the remaining 9.6% were tea houses and coffee bars. Using the information shown in Table 3, a value of 4124.33 ± 120.47 t $Yr^{-1}$ was obtained for the annual total VOC emissions derived from cooking. The annual NMHC was found to be 6698.96 ± 605.41 t $Yr^{-1}$.

### 3.6. VOC emission inventories based on restaurant scales

To estimate annual VOC emissions from restaurants in Shanghai based on restaurant scales, barbecue, fried food and family kitchens were not considered here, mainly because their operating modes are flexible, rendering them difficult for urban governance.

The emission factors shown in Table 2 were employed in the calculations. All parameters and the annual amount of VOC and NMHC emissions based on restaurant scales are listed in Table 3.

The calculated annual amount of VOC and NMHC emissions based on restaurant scales by Eqs. (8)–(10) were less than those based on cuisine types for all three emission factors. One reason for this difference is the same as the interpretation given previously, that barbecue, fried food and family kitchens were not considered. Another reason for this difference is attributed to the smaller variances of EF among restaurants of the same scale. Large and medium-sized restaurants are with high emission factors and high emission concentrations, which are also easier to be managed in comparison to small restaurants and barbecue.

The results obtained by three proposed methodologies were as follow: $S_{hour-type} < S_{kitchen\ stove-type} < S_{person-type}$ and $S_{kitchen\ stove-scale} < S_{hour-scale} < S_{person-scale}$. The $S_{person}$ was the highest for both methodologies. The more accurate the survey results, the closer the results obtained from the three methodologies will be.

### 3.7. Geographical distribution of the intensity of VOC and NMHC emissions produced by cooking in urban Shanghai

According to the annual total VOC emissions calculated from restaurant scales, the geographical distribution of the intensities of VOC and NMHC emissions produced by cooking in Shanghai in 2012 are shown in Fig. 6. Although Pudong and Minhang districts had the highest annual total VOC or NMHC emissions, the largest emission intensities appeared in Huangpu, Jing'an and Hongkou districts, which are located in urban centers – the emissions per unit area are larger than all other districts.

### 3.8. Geographical distribution of the annual total amount of VOC emissions produced by cooking in China

Environmental Kuznets Curve (Dinda, 2004) indicates the economic capacity has a positive correlation with pollutant emissions prior to economy developed into a certain level, which presents an approximate linear relation. China is a developing country, which is located before the turning point in the curve. Therefore, according to the obtained yearly VOCs emissions of 100,000 people from catering business ($S_{hour\text{-}scale}$/Shanghai population ∗ 100,000people), Shanghai catering consumption ability (as shown in Table SI4), and national catering consumption ability in China, the yearly VOCs emissions of 100,000 people in different provinces were obtained as Fig. 7(a). According to this general linear relationship and consumption and emissions of Shanghai catering, and other areas' consumption of catering, we can get the general emissions of other regions. It can be illustrated that VOCs emissions of 100,000 people from catering business in four municipalities are over 6 t/year·100,000 people. Shanghai reached up to 8.16 t/year·100,000 people. Tianjin is the highest one among four municipalities, attaining to 11.23 t/year·$10^5$ people. In addition, greater VOCs emissions of 100,000 people mainly occurred in provinces with high floating population and rich tourism resources. And furthermore, the yearly VOCs emissions of each province in China were obtained, as given by Fig. 7(b). Shangdong and Gungdong provinces have the highest VOCs emissions, reaching up to 5680.53 t/year and 6122.43 t/year, respectively, nearly three times of Shanghai. The annual amount of VOCs emission from catering industry in China is 66,244.59 t/year, and 4.79 t/year·100,000 people. The total annual VOCs emission is not only related to populations of different provinces, but also associated with local eating habits and economic conditions.

### 3.9. Importance of barbecue emissions as a source of health hazards

Considering the VOCs concentrations of barbeque emissions was the greatest in this study, and it is also the source nearest to the ground, hence its potential health effect are discussed. Acetaldehyde is classified as a group 2b carcinogen (possibly carcinogenic) by International Agency for Research on Cancer (IARC), with a limiting value of 0.003 mg/$m^3$. But the acetaldehyde concentration emitted from barbeque was 0.34 ± 0.07 mg/$m^3$ in this study. The monitored hexanal concentration was 0.26 ± 0.02 mg/$m^3$, up to 8 times of the limiting value of 0.03 mg/$m^3$ set by German statutory accident insurance. Australian government and U.S Environmental Protection Agency (EPA) sets the limiting values of acrolein in workplaces as 0.23 and 0.24 mg/$m^3$, respectively. The monitored acrolein concentration was 0.24 ± 0.04 mg/$m^3$ from barbeque emissions in this study.

## 4. Conclusions

This research sheds light on the significance of cuisine types and restaurant scales on VOC compositions, and their resulting chemical reactivities, that are entering into urban atmospheres from cooking emissions in Shanghai. Our results showed that alkane and oxygenated VOCs (O-VOCs) account for 51.26% ± 23.87% and 24.33 ± 11.69%, respectively to the VOC emissions produced by cooking. Yet, the VOCs with the largest OFP and SOAP were from the alkene (6.78–96.95%) and aromatic (73.75–98.86%) categories, respectively. Barbeque has the most potential of harming people's heath due to its significant higher emissions of acetaldehyde, hexanal, and acrolein.

The estimated annual total amount of VOCs is 4124.33–7818.04 t/year and 1355.11–2402.21 t/year based on $S_{type}$ and $S_{scale}$, respectively. The VOCs emission of 100,000 people from catering business is 8.16 t/year·100,000 people in Shanghai. Shangdong and Guangdong provinces reach up to 5680.53 t/year and 6122.43 t/year, respectively. And the VOCs emission from catering industry in China is 66,244.59 t/year, and 4.79 t/year·100,000 people.

The quantitative analysis of this research calls the attention of regulating authorities by providing them with the information needed to evaluate the major factors impacting on VOCs from cooking emissions in Shanghai as well as the whole nation. We suggest that large and medium-scaled restaurants should be regarded as the most important with respect to regulation of VOCs, and street barbeque should be taken seriously for its potential health hazard. The conclusions provide the foundation for building a continuing body of statistical knowledge and methodologies that can be used in calculating emission factors, inventories, and total annual amount for other cities and nations, as well as for assessing the impact of cooking emissions on urban atmosphere and human health.

## Notes

The authors declare no competing financial interest.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2017.10.098.

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