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Original Research

## VOCs evaporative emissions from vehicles in China: Species characteristics of different emission processes



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### ABSTRACT

Vehicle evaporation is an essential source of VOCs in cities but is not well understood in China. Reported emission factors from previous studies are not enough for understanding the atmospheric chemical process of vehicular evaporative VOCs. In this work, a series of detailed VOCs speciation profiles are developed based on test processes and emission processes. A mass balance method was used to divide different emission processes during diurnal tests. The results show that headspace vapor of gasoline cannot represent the real-world vehicle evaporation because of the significant differences in VOCs speciation profiles, especially for aromatics. To further distinguish emissions from evaporation and exhaust, only the ratios of MTBE/benzene and MTBE/toluene can serve as indicators when considering species from all evaporative processes. Besides, emissions from different sources change significantly with the seasons. To solve these problems, we developed a monthly comprehensive evaporation speciation profile. The individual profiles at the emission processes are weighted by the emission of the in-use vehicle fleet in Beijing to derive the comprehensive speciation profile of evaporative VOCs. Ozone formation potential (OFP) and secondary organic aerosol potential (SOAP) were used to evaluate the environmental impact. For SOAP, 100 g evaporative emissions are equal to 6.05–12.71 g toluene in different months, much higher than that given using headspace vapors, especially in winter (7.2 times higher in December). These findings would improve our understanding of the evaporative VOCs emissions in China and their environmental impacts (e.g., O<sub>3</sub> and SOA formation).

### 1. Introduction

Vehicle-related emissions are widely recognized as the primary source of anthropogenic volatile organic compounds (VOCs) in urban areas [1–4]. This has been proved to have significant impacts on air quality and public health [5–8]. VOCs emissions from motor vehicles are generated through several pathways that can be grouped into tailpipe emissions (or exhaust) and non-tailpipe (or evaporative) emissions. Previous studies on gasoline vehicle-related emissions have mainly focused on the emission factors, speciation, and inventories of tailpipe VOCs emissions [9–14]. For evaporative emissions, several test programs in the United States of America (USA) have investigated the amount of

evaporative VOCs emissions from Tier 0 to Tier 2 vehicles [15,48,49]. Pang et al. evaluated the trends of evaporative emissions in the USA based on 49 in-use vehicles with the model year between the 1999 and 2003 fleets [16]. Mellios et al. tested four vehicles in Europe to validate their evaporative emissions [17]. Yamada et al. [18] and Hata et al. [19] estimated the evaporative emission of Japan based on several tests results and theoretical model. In China Liu et al. [20] and Man et al. [21] provided detailed estimates of the VOCs evaporative emissions from different processes, including diurnal, hot soak, refueling, and permeation. They found that evaporative emissions are becoming increasingly crucial to total VOCs emissions in China [20].

Compared to the emission factor studies mentioned above, research

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on vehicular VOC speciation is far from enough. Studies of atmospheric chemistry generally use the speciation of headspace vapors and liquid fuels to represent that of the evaporated VOCs from vehicles [22–26]. Schifter et al. [27] and Yamada et al. [18] analyzed VOCs species from diurnal emissions to provide real-world VOCs speciation profiles for this particular process. Their results showed that the VOCs speciation profiles were significantly different from those of headspace or liquid fuels. Although there are more studies in the USA that investigated the VOCs species of evaporative emissions [16,48,49], the results cannot be simply applied to other countries because of the distinct differences in-vehicle technologies and gasoline formulas [20]. Besides, nearly all previous studies give species profiles based on the test process, e.g., refueling, diurnal, hot soak, rather than distinguishing VOCs speciation profiles according to different evaporative processes, e.g., static permeation, venting permeation, hot soak, and venting carbon canisters, refueling. The absence of a process-based speciation profile was an obstacle for evaluating overall speciation for vehicle fleet using limited test samples.

VOCs speciation profiles are critical for both scientific researches and air quality management practices. The lack of detailed information on VOCs species has limited our understanding of the sources' contributions to ambient VOCs [28]. Using a positive matrix factorization (PMF) model without source profiles, Song et al. reported an evaporation-to-exhaust ratio of ~0.3 for VOCs in Beijing during 2006–2007 [29]. Using similar method, Yuan et al. reported this ratio to be 1.11 in Beijing in 2010 [30]. Wang et al. reported a ratio of 0.133 in Beijing during 2009–2011 using headspace profiles as the source profiles of evaporation in the chemical mass balance (CMB) method [31]. The significant discrepancies among these studies show the large uncertainties of vehicular evaporative emissions. The uncertainties may come from the differences in methodologies and/or the absence of evaporation VOCs profiles because the contribution of different evaporative processes would change when temperature and car-use changes. Especially, the composition of overall evaporative emission would change along with seasons and locations. Then, using one species profile to represent a variable evaporative process would bring significant uncertainty to source apportionment and the evaluation of evaporative emissions. If a comprehensive speciation profile of vehicle evaporation can be determined and used in source apportionment, the shares of evaporation and exhaust will be more convinced, and the source apportionment results will provide more information to evaluate control effects of vehicle exhaust, as well as other sources, on VOCs emissions.

Compared to our previous study on emission amounts [20], this study aims to provide necessary information for understanding the atmospheric chemical impacts from vehicular evaporative emissions. The targets of this work include obtaining a VOCs speciation profile of the comprehensive process of evaporation instead of vapors only, identifying the indicators to distinguish evaporation from the exhaust, estimating the ozone formation potential (OFP) and secondary organic aerosol (SOA) yields of evaporation. The first target is to obtain representative VOCs speciation profiles for vehicle evaporative emissions in China. Achieving this, a series of VOCs samples of vehicular evaporative tests are measured, including refueling, hot soak, and diurnal test processes. Based on modeling results, the weight of different emission processes to a single test process is determined. Combining the first and the second steps, profiles for emission processes were further provided. The detailed VOCs speciation profiles of five emission processes are then weighted by emissions of corresponding processes to derive the comprehensive monthly VOCs speciation profile of vehicular evaporative emissions in Beijing. We further identify several indicators using ratios of several components to distinguish emissions from evaporation and exhaust. The impacts on ozone and SOA formation of the comprehensive speciation profiles are also studied and compared with the previous studies.

## 2. Method

### 2.1. Test procedures

For the test processes, according to EPA standard test procedures [32] and previous research program (CRC\_E-65-3) [49], evaporative emissions could be divided into refueling, hot soak, permeation, and diurnal tests in this study. For emission processes, the refueling process is the vapor in the fuel system that is displaced into the atmosphere as a vehicle refuels and spillage; permeation is the vapor permeates from the whole fuel system and could be divided into static permeation and venting permeation; hot soak is the vapor emitted from the fuel system when the engine is still hot. While, during the diurnal process, there are two emission processes occurred at the same time: permeation and venting of the canister. Then, the actual species profiles of diurnal emissions were concerned with the distribution of these two mechanisms during diurnal tests.

In this study, we conducted 35 crossover tests on five test vehicles in a gas-tight Imtech variable-temperature Sealed Housing for Evaporative Determination (VT-SHED) chamber in Beijing China (Table S1). Two US Tier 2 vehicles and three Euro 4 vehicles (equivalent to China 4) were tested. The three Euro 4 vehicles were selected from the most popular vehicle brands, and models dominated car sales in China in 2013. The main difference between US Tier 2 and Euro 4 vehicles is the vapor control technology: Onboard Refueling Vapor Recovery (ORVR) for US Tier 2, whose control efficiency could reach over 98% for refueling and diurnal tests [20], and conventional 24-h diurnal control for Euro 4. Detailed vehicle information is listed in Table S2.

Detailed procedures for all tests are described in Table S3 [32–34]. US refueling test were chosen to determine the VOC speciation profiles of refueling [32]; and the US 48-h diurnal test, US 72-h diurnal test [32], and China 24-h diurnal test [34] were all conducted to determine the diurnal profiles. Hot soak tests were conducted before both Euro 4 and Tier 2 diurnal tests.

Because the emissions in the VT-SHED consist of not only vapor diffusion through plastics and elastomers in pipes, fittings, and fuel tanks, but also leaks and evaporation from other parts, e.g. seats of the vehicles [35], each car was checked carefully before the test to minimize the leaks and evaporation from other parts. At the current stage, the uncertainty of this could not be determined. So, we also conducted a constant temperature permeation test to verify the static permeation first. And, canister emissions and venting permeation would be divided from the results of diurnal tests based on mass balance.

The fuel used in this study was certification gasoline from Sinopec, the largest supplier of gasoline in China (more than 47% Chinese market share in 2018). The formula and parameters of this certified fuel were the same as the market requirements (Table S4). For example, Reid vapor pressure (RVP), the most important gasoline parameter for evaporation, was 58 KPa, meeting the market gasoline requirement of 55–65 KPa. The RVP value is comparable to that in Europe, where the fuel RVP is currently required to be in the range of 56–60 KPa. A survey conducted in Beijing also indicated that the RVP of gasoline fuel was in the range of 47.0–56.8 KPa during 2013 (Table S5).

### 2.2. Sample analysis

A flame ionization detector (FID) was recalibrated before each measurement and was then used to measure total hydrocarbons (THC) concentrations in the VT-SHED chamber. A fan in the VT-SHED chamber mixed the air to homogenize the concentration. Simultaneously, the gas samples in the VT-SHED chamber were collected using 3.2 L summa canisters (Entach Instruments, USA). The average flow rate of the summa canisters was approximately 250 mL/min, and the sampling duration was approximately 12 min. In total, 63 samples were collected, including 33

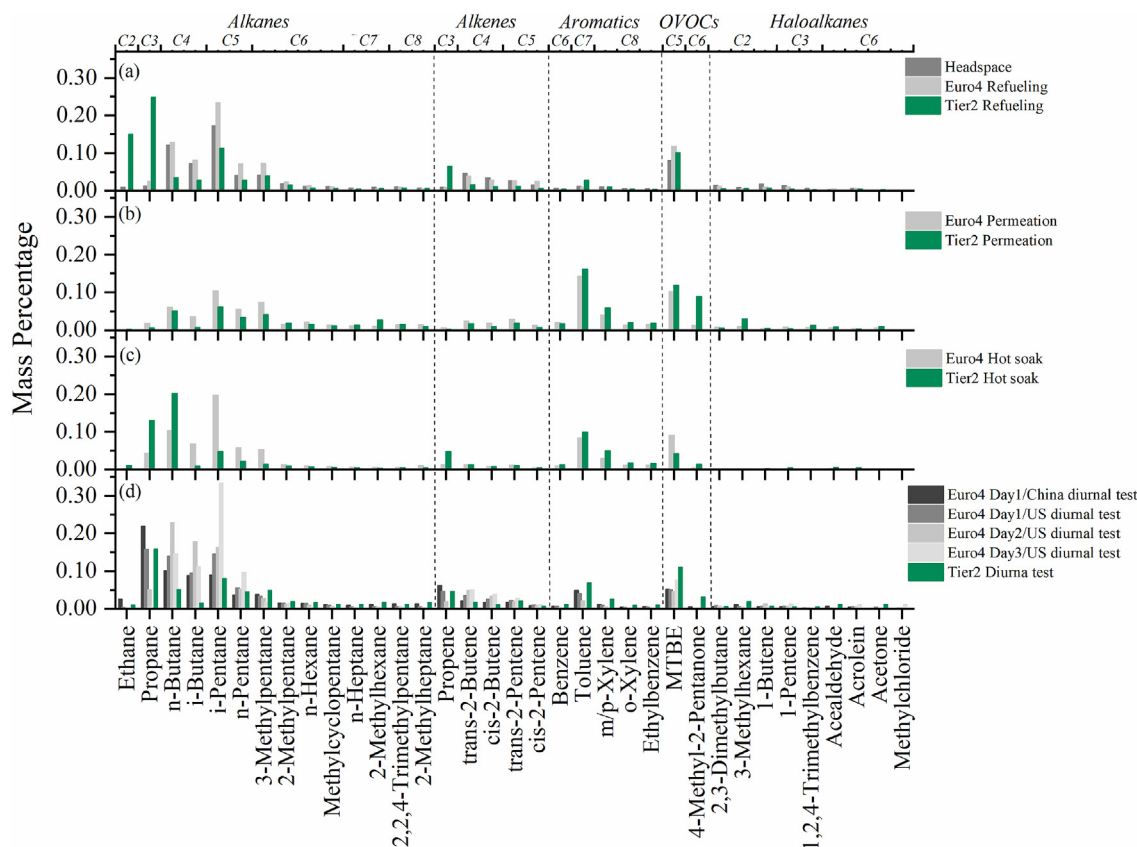


Fig. 1. Weight percentage of 35 main species from different test processes using Euro 4 and Tier 2 vehicles.

samples for diurnal emissions, 10 for refueling missions, 12 for permeation emissions, 7 for hot soak emissions, and 1 for headspace vapors. Compared with other analogous researches [9,36,37], numbers of test vehicles and samples were quite competitive (Table S6). The samples were analyzed using an Entach 7100 three-stage cryofocusing pre-concentration system (Entach Instruments, USA) and a gas chromatography-mass spectrometry (GC-MS, 7890A, Agilent, USA) instrument with an FID. The GC-MS parameters and quality assurance (QA/QC) procedures used in this system were the same as those employed in previous studies [26,50,38]. In total, approximately 90 organic species were detected.

### 2.3. Calculation of OFP and SOAP

The environmental impact of vehicular VOC evaporations was further assessed based on OFP and SOA yields [6]. And, the MIR method is widely used to calculate the ozone formation potential. We calculate the OFP by combining the VOC speciation profiles obtained in this study and the corresponding maximum incremental reactivity (MIR) (SAPRC) [50].

$$\text{OFP}_j = \sum w_i \times (\text{MIR})_i$$

where  $\text{OFP}_j$  is the ozone formation potential for profile  $j$  ( $\text{g O}_3/\text{g VOCs}$ );  $w_i$  is the weight percentage of species  $i$ ;  $(\text{MIR})_i$  is the MIR of species  $i$  ( $\text{g O}_3/\text{g VOCs}$ );

SOAP was defined as the propensity of each organic compound to form SOA on an equal mass emitted basis relative to toluene [39]. SOAP for species  $i$  is defined as the following equation:

$$\text{SOAP}_i = \frac{\text{Increment in SOA mass concentration with species } i}{\text{Increment in SOA with toluene}} \times 100$$

SOAP of different evaporative emissions profiles was calculated using

the following equation:

$$\text{SOAP}_j = \sum \text{SOAP}_i \times w_i$$

where  $\text{SOAP}_i$  is the SOA yield potential of species  $i$  (unitless);  $\text{SOAP}_j$  is the SOA yield potential of profile  $j$  (unitless);  $w_i$  is the weight percentage of species  $i$ .

## 3. Results and discussion

A series of VOCs speciation profiles of vehicular evaporative emissions are provided according to test processes and emission processes. Totally, we identified 35 main VOCs species for evaporative emissions, accounting for 80.55%–98.64% of the total amount of detected organics. Alkanes are the most abundant structural group for nearly all types of evaporation, ranging from  $38.41 \pm 3.24\%$  (Tier 2 vehicle, permeation tests) to  $75.65 \pm 2.55\%$  (Euro 4 vehicle, Day 2/US diurnal tests). Haloalkanes account for only 1.13% on average, and alkynes were hardly detected for all tests. Aromatics show the largest rangeability ( $1.4 \pm 0.6\%$  to  $26 \pm 8\%$ ). Detected species and their share are listed in detail in Table S7. The VOC speciation profiles from different test processes and different emission processes would be discussed in the following sections.

### 3.1. VOCs speciation profiles of different test processes

#### 3.1.1. VOCs speciation profiles of refueling tests

As the refueling emission is the fuel vapors pushed out of the fuel tank when liquid fuel is added to the tank. Then the VOCs speciation profile of the refueling process is very similar to the headspace vapors for Euro 4 vehicles. These vehicles could represent the major fleet without ORRV technology in the China market (Fig. 1 and Fig. 2). Alkanes, alkenes, aromatics, and oxygenated volatile organic compounds (VOCs) account for  $70.54 \pm 2.82\%$ ,  $14.52 \pm 3.66\%$ ,  $1.43 \pm 0.60\%$  and  $13.04 \pm 6.34\%$ ,

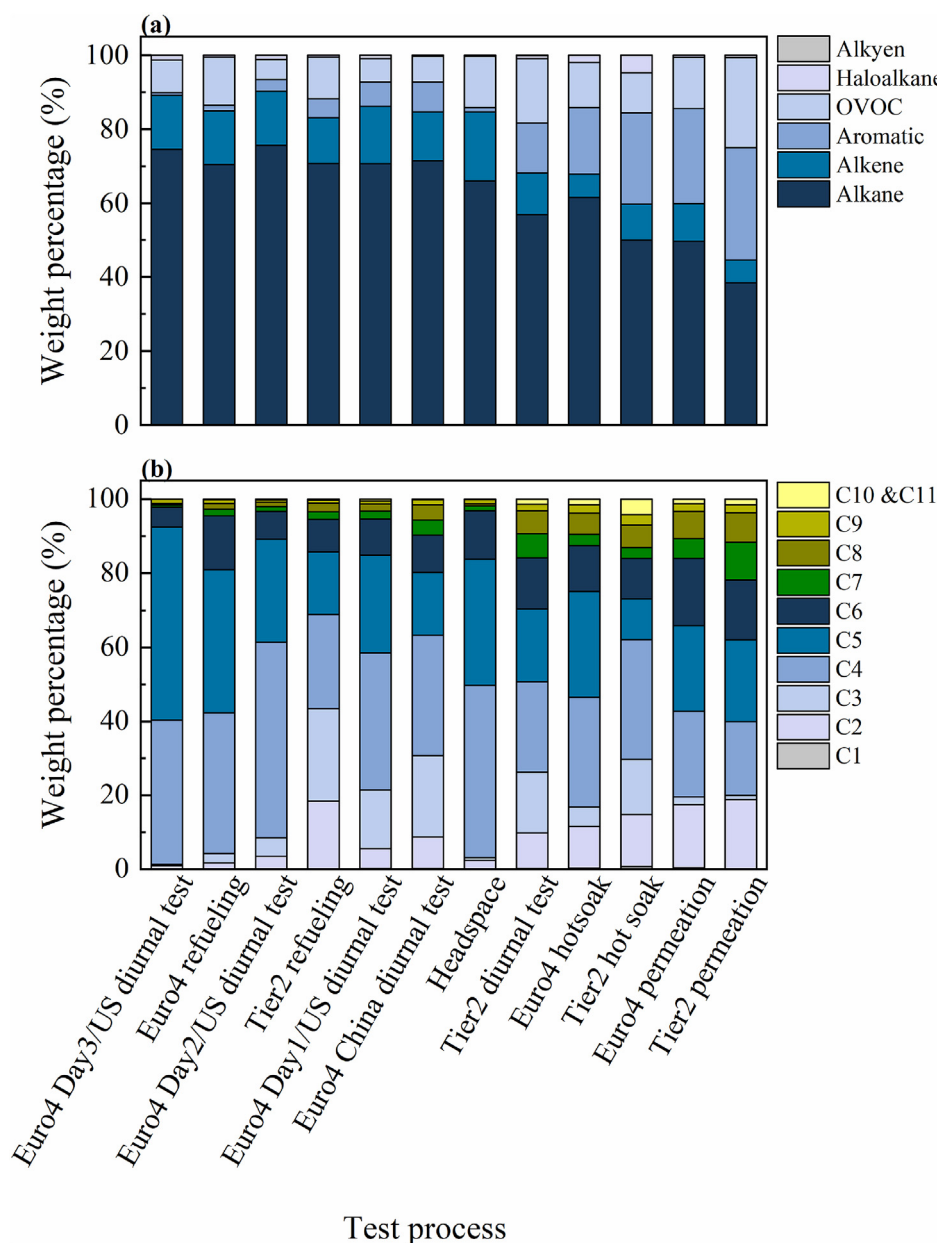


Fig. 2. Weight percentage of VOCs composition by group (a) and by carbon number (b).

respectively, of the refueling emissions, and 66.00%, 18.72%, 1.13%, and 13.83%, respectively, of the headspace vapors. For carbon number distribution, those of refueling emissions from Euro 4 vehicles and headspace vapors are quite similar. From aspects of major species, *i*-pentane ( $23.3 \pm 4.09\%$ , 20.01%), *n*-butane ( $12.82 \pm 4.30\%$ , 16.98%), methanol/methyl *tert*-butyl ether (MTBE) ( $11.71 \pm 5.82\%$ , 12.31%), *i*-butane ( $8.08 \pm 0.55\%$ , 8.93%), 3-methyl pentane ( $7.31 \pm 1.48\%$ , 6.52%), *trans*-2-butene ( $3.80 \pm 0.44\%$ , 5.49%), and *n*-pentane ( $7.13 \pm 0.51\%$ , 4.79%) are the main components of both the refueling emissions and the headspace vapors, accounting for 75.03% and 74.11%, respectively (Fig. 1). Pearson's correlation coefficient (Table S8) between the two speciation profiles (refueling for Euro 4 vehicles vs. headspace) is 0.979 ( $P < 0.001$ ,  $N = 97$ ). The high correlation verified that the displacement of vapors in the fuel tank (i.e., the mechanism of venting) is the main source of the refueling VOCs emissions. Compared to headspace vapors in other countries, refueling emissions in China have more aromatics, e.g., 9.34% in China versus 2.86% in the USA [25] and 1.62% in Korea [40]. The species profile of headspace vapors is mainly concerned with the

components of fuel. Then, this difference is probably attributed to the high proportion of aromatics in Chinese gasoline (41.38% V/V) (Fig. S1), which is 1.50 times higher than in the US [6]. In essence, the species of refueling emissions from Euro 4 vehicles represent the characteristic of evaporative emissions directly from the interior space of the fuel tank.

However, the refueling speciation profiles of US Tier 2 vehicles (with ORVR) differ considerably from those of the Euro 4 vehicles (Fig. 1). Though percentages of alkanes ( $70.76 \pm 1.24\%$ ), alkenes ( $12.31 \pm 1.81\%$ ), aromatics ( $5.24 \pm 0.67\%$ ) and oxygenated volatile organic compounds (OVOC,  $11.2 \pm 0.4\%$ ) are similar to Euro 4 vehicles, the dominant species diverse a lot. For refueling emissions from Tier 2 vehicles, propane, ethane, *i*-pentane, and MTBE are the main components, accounting for  $61.1 \pm 4.3\%$ . The weight percentage of VOCs with low carbons (<5) is  $57.1 \pm 9.0\%$ , much larger than those of headspace and refueling emissions from Euro 4 vehicles. The differences are mainly because US Tier 2 vehicles are equipped with ORVR devices, which could remove  $\sim 99\%$  of the refueling VOCs emissions [20]. Under the full control of ORVR devices, the differences in the carbon adsorption

efficiency among different VOCs species dominant the measured VOCs profile, making the speciation profiles of the refueling processes of the US Tier 2 vehicles differ from those of headspace vapors and Euro 4 vehicles. So, using species profiles of headspace vapors could only reflect parameters of refueling emission from vehicles without ORVR. When the new standard implied, this would not work anymore.

### 3.1.2. VOCs speciation profiles of hot soak tests

Hot soak is 1-h emission after the engine shut down, being the vapor emitted from the fuel system when the engine is still hot. The difference between hot soak emission factors of Euro 4 and Tier 2 vehicles is very tiny (Fig. 1). Alkanes, alkenes, aromatics, and OVOCs account for 55.76%, 8.08%, 21.31% and 11.52% on average. Though alkanes were still the dominate category, the weight percentage of aromatics reached over 20%. Though a portion of *n*-butane, *i*-pentane, and MTBE was also still high (34.11% on average), the weight percentage of toluene reached over 8%, much higher than headspace vapors. For the chemical reactivity in the atmosphere of aromatics is higher than alkanes [6], the impact of hot soak emissions would be underestimated when using species profile measured from headspace vapors.

### 3.1.3. VOCs speciation profiles of permeation tests

Permeation is the vapor that permeates from the whole fuel system. When the temperature outside is constant, the main mechanism of emissions is the Brownian diffusion. Otherwise, when the temperature rises, gas in the fuel system expands, venting occurs. During the temperature-rise period, permeation emission is the combination of static permeation and venting permeation. For evaporative VOCs emissions through the permeation mechanism, the weight percentage of aromatics is high, reaching  $30 \pm 4\%$  and  $26 \pm 8\%$  for the studied Euro 4 and US Tier 2 vehicles, respectively (Fig. 2). High aromatic concentrations ( $\sim 25\%$ ) have also been found in Japan for permeation [18]. Toluene is the most abundant species, reaching  $14.19 \pm 4.05\%$  and  $16.06 \pm 1.17\%$  for Tier 2 vehicles and Euro 4 vehicles, respectively. The emissions are affected by the permeability of materials. Aromatics migrate more easily through the wall of the fuel system, and this is the reason why the proportions of aromatics in the permeation mechanism are ten times higher than in the venting mechanism. Our previous study [20] reported that permeation emissions are a significant contributor to total evaporation emissions. Therefore, the speciation profile of permeation emissions could have a significant influence on the average speciation profile of the total evaporation emissions.

### 3.1.4. VOCs speciation profiles of diurnal tests

We find considerable variations in the diurnal VOCs speciation profiles among the Euro 4 vehicles but only minor variations among the US Tier 2 vehicles. Therefore, we introduce the measurement at another two levels (i.e., emission composition and species composition) to explore the reasons. The contributions of the individual processes to the speciation profiles of diurnal processes are determined via the control technologies of the test vehicle.

There are significant differences in control efficiency of diurnal emissions among different emission control technologies: (42%–96%) among Euro 4 cars and (98%–99%) among US Tier 2 vehicles [20]. The control efficiency of Euro 4 cars varies with the test procedure. It reached up to  $95.2 \pm 0.4\%$  during the Euro-type IV test. So, all results from the Euro-type IV test were defined as under efficient control. The overall control efficiencies during diurnal tests changed from  $\sim 95\%$  to  $\sim 60\%$  for US 48 h and 72-h tests. Then, from the first day to the third day of the US diurnal tests, the control condition changes from limited control to no control. For Tier 2 vehicles, no further classification is necessary because ORVR captured nearly all vapors under these tests. Thus, the diurnal emissions from Tier 2 vehicles can be treated as diurnal under efficient control.

The dominant emission process changes with the emission control efficiencies. From efficient control to non-control, the possibility for

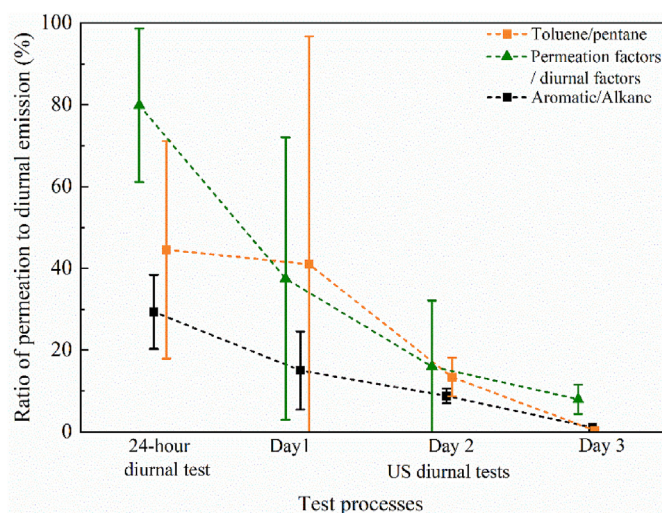


Fig. 3. Indicators of processes for diurnal emissions.

venting of carbon canister increase, and the possibility for permeation decreases. This mechanism changes lead to an increase in emissions from  $0.834 \pm 0.164$  g/day to  $8.144 \pm 1.989$  g/day. The weight percentage of aromatics decreased from  $14 \pm 4\%$  to  $5 \pm 4\%$ . Toluene, the most abundant aromatic for permeation, decreased from 4.82% to 0.32%. And the average ratios of aromatics/alkanes and toluene/pentane decreased from 29.4% and 44.6% to 1.1% and 0.4%. And the ratios of permeation emission factors versus diurnal emission factors decreased from 79.9% to 8.0% (Fig. 3). From efficient to no control, these ratios decrease, indicating venting instead of permeation mechanism becomes dominant. Error bars reflect the differences among the studied vehicles. For efficient control and limited control conditions, different carbon canisters lead to very large emission variations. For no control and little control, nearly all vapors are released; thus, the differences between individual vehicles are smaller.

From the aspect of the test process, we could not divide species profiles of venting permeation and venting of the canister. A regression method was used to research the individual species profile of the emission process from mixed diurnal emission profiles.

### 3.2. VOCs speciation profiles of different emission processes

Results of refueling tests, hot soak tests, and permeation tests could reflect the characteristics of species for the refueling process, hot soak process, and static permeation tests. While, for diurnal tests, venting canister, venting permeation, and static permeation occurred at the same time. Then, the actual species profiles were concerned with the distribution of these three emission processes during diurnal tests. There was a mass balance for the weight percentage of species.

$$C_{i,j} = k_{per,j} \times C_{per,i} + k_{vper,j} \times C_{vper,i} + k_{can,j} \times C_{can,i}$$

Where  $C_{i,j}$  is the weight percentage of specie  $i$  during diurnal test  $j$ ;  $k_{per,j}$ ,  $k_{vper,j}$ ,  $k_{can,j}$  were the portion of static permeation, venting permeation, venting canister during diurnal test  $j$ ;  $w_{per,i}$ ,  $w_{vper,i}$ ,  $w_{can,i}$  were the weight percentage of species  $i$  in species profile of static permeation, venting permeation, and venting canister.  $k_{per,j}$ ,  $k_{vper,j}$ ,  $k_{can,j}$  were calculated using measured emission factors combined with evaporative models. Fig. 4 is the emission composition during diurnal tests. Species of diurnal tests measured with Euro4 vehicles were used to calculate species profiles of venting permeation and venting canister. Leave-one-out cross-validation (LOOCV) was used to verify the results (Fig. 5).

Table 1 lists the comparison of the five emission processes from major species, the weight percentage of major species, ratios of species categories, carbon number distribution of species, OFP, and SOAP. Butane

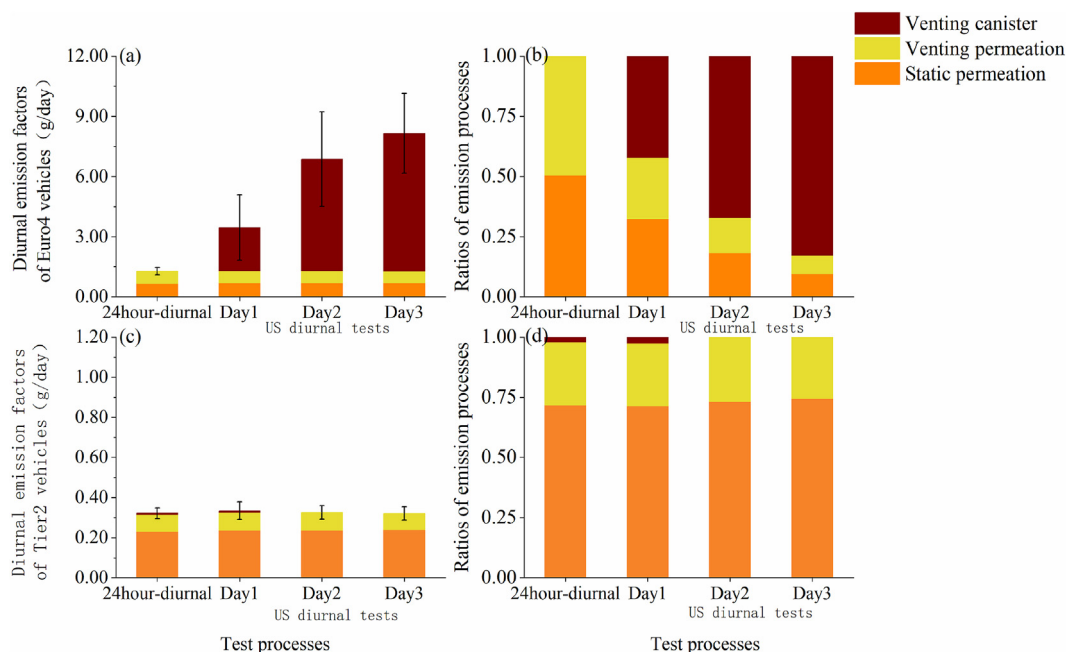


Fig. 4. The emission factors and ratios of three emission processes during diurnal tests of Euro 4 vehicles and Tier 2 vehicles.

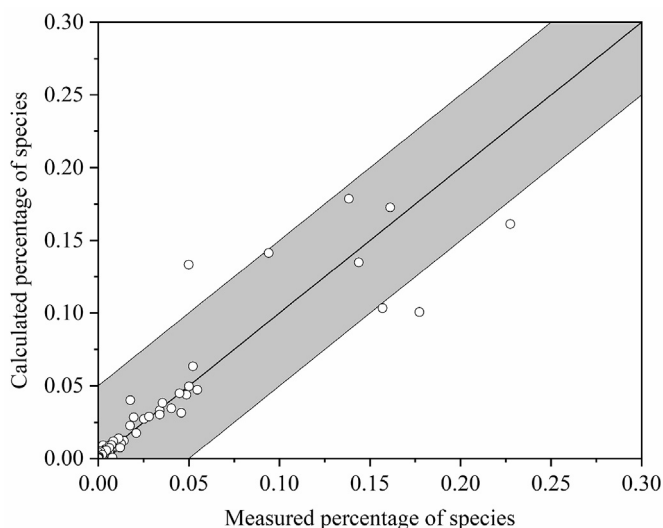


Fig. 5. Comparison of species measured in tests and calculated using the calculated emission process profile.

Table 1

Characteristics of species from different emission processes.

Emission process	Refueling	Hot soak	Statistic permeation	Venting permeation	Venting canister
Major species	<i>i</i> -Pentane <i>n</i> -Butane MTBE <i>i</i> -Butane 3-Methylpentane <i>n</i> -Pentane <i>trans</i> -2-Butene	<i>i</i> -Pentane <i>n</i> -Butane MTBE Toluene <i>i</i> -Butane <i>n</i> -Pentane 3-Methylpentane	Toluene <i>i</i> -Pentane MTBE 3-Methylpentane <i>n</i> -Butane <i>n</i> -Pentane <i>m/p</i> -Xylene	Propane <i>n</i> -Butane <i>i</i> -Butane Propene <i>i</i> -Pentane Ethane <i>n</i> -Pentane	<i>i</i> -Pentane <i>n</i> -Butane <i>i</i> -Butane Propane <i>n</i> -Pentane <i>trans</i> -2-Butene MTBE
Portion of major species	74.11%	64.90%	57.24%	86.33%	75.28%
Alkanes: Alkenes: Aromatics: OVOCs	70:14:1:13	61:6:18:12	50:10:26:14	84:14:0:1	73:18:2:5
C <sub>2</sub> -3:C <sub>4</sub> -5:C <sub>6</sub> -11	4:77:19	16:58:25	19:46:34	42:48:10	12:78:9
OFP	2.96	2.80	3.47	2.54	3.30
SOAP	1.92	1.77	25.08	0.36	2.40

and pentane are the major species for all evaporative emission processes. The detailed species of the five emission processes were listed in Table S9. The distribution of species from static permeation was the most decentralized, the first seven species only contributing 57.24%. Comparing to other processes, species of venting permeation were more concentrated and had more species with lower carbons, the carbon number of 42% species lower 4. The maximal seven species of venting permeation (propane, *n*-butane, *i*-butane, propene, *i*-pentane, ethane, *n*-pentane) contributed 86.33%. The portion of Alkanes researched 84%, much higher than static permeation and other emission processes. Species of venting canister were similar to those from Euro 4 refueling tests. That is because the canister breaks through during diurnal tests of Euro 4 vehicles [20]. Then, most vapors venting from the canister were just the headspace vapors in the fuel tank, similar to refueling emissions.

The OFP of species measured during different test processes ranged from 2.478–3.539 g O<sub>3</sub>/g VOCs (Fig. 6). The average OFP of different evaporative emissions processes was 3.013 ± 0.335 g O<sub>3</sub>/g VOCs. Though the difference of OFP between different test processes or emission processes was not very large, the contributor of OFP quite different. Aromatics contributed about 40% OFP of static permeation, while

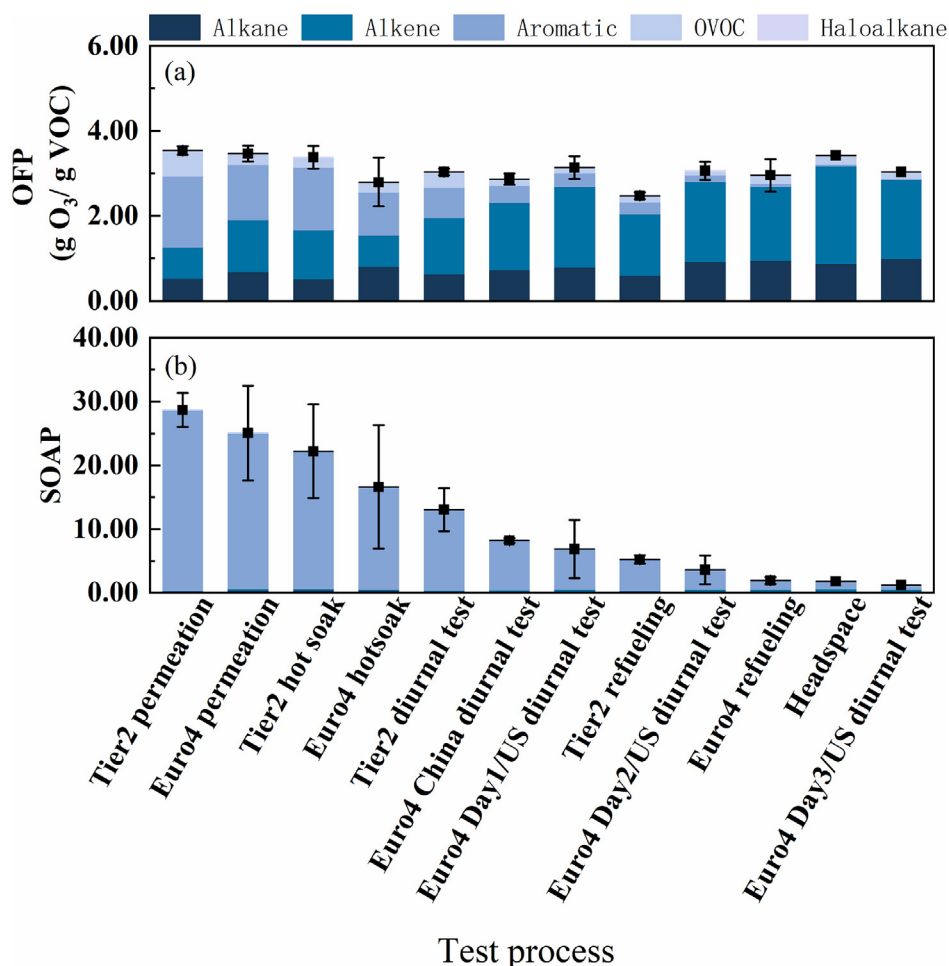


Fig. 6. OFP (a) and SOAP (b) of vapors from different test processed.

alkenes were the key contributor to venting processes (venting permeation, venting canister). The evaporations present comparative OFP levels compared to the OFP of exhaust VOCs emissions ( $3.53 \pm 0.08$  g O<sub>3</sub>/g VOCs) [41]. Besides, the OFP values of evaporative VOCs in China are much higher than those reported in the US (e.g., 1.61 g O<sub>3</sub>/g VOCs for headspace vapors, [25]). Thus, our detailed evaporative VOCs speciation profile could serve to update the emissions inventory in China.

The SOAP ranged from 0.359–25.078 for different processes. As C<sub>2</sub>–C<sub>6</sub> VOCs contribute more than 90% of venting processed emissions, the SOAP of venting canister, refueling, or Euro 4 diurnal tests was quite low. Species of static permeation also presents the highest SOAP among all emission process because of the high percentage of aromatics. Then, the environmental impact of specific mass evaporative emissions determined by the emission process composition.

### 3.3. VOCs speciation profiles of evaporative emission in Beijing

As mentioned above, VOCs speciation profiles vary significantly for the different evaporation processes. We estimated the evaporative emissions based on spatial and temporal car-use big data and meteorological conditions in our previous study [42,43]. The average evaporative emission factors during parking in Beijing were divided into refueling emissions, hot soak emissions, static permeation, venting permeation, and venting of the canister. The average emission factors for parking evaporative emissions was 0.443 g/(day vehicle) in December and reaching 3.800 g/(day vehicle) in July. On average, the weights of the refueling emissions, hot soak emissions, static permeation, venting permeation, and venting of the canister exhibit a ratio of

12.81:14.08:18.37:10.61:44.11. While venting canister was dominated process in Summer, reaching 64.57% in July. The ratio of static permeation was high in spring or autumn, more than 20% in March and September to October. In winter, the low temperature leads to the decrease of vapor generation, and hot soak becomes significant, nearly a half.

Here, we develop a comprehensive monthly speciation profile in Beijing based on the emission processes profiles obtained in previous sections and their contributions to the total evaporative emissions in the Chinese vehicle fleet. (Fig. 7). *i*-Pentane (16.43–18.01%) and *n*-butane (10.74–15.36%) were the dominant species in all month. Percentages of aromatics, such as toluene, alkenes, such as *cis*-2-butene and *trans*-2-butene, nearly doubled from summer to winter. Comparing the comprehensive VOCs speciation profile to the profile of headspace vapors, aromatics, ranged from 5.80% to 13.28%, 5 to 12 times higher than headspace vapors.

Because the OFP of species from different test processes or emission process change little ( $3.10 \pm 0.32$ ), the OFP of the comprehensive profile is also similar. The average OFP of species in different months is  $3.08 \pm 0.08$  g O<sub>3</sub>/g VOCs.(Fig. 8 a), but the impact of vehicle evaporative emissions on ozone formation in July would be 8 times higher than that in January. (Fig. 8 b). The SOPA of constant evaporative emissions varies significantly in different seasons. One hundred grams of evaporative emissions are equal to 6.05–12.71 g toluene in different months. This value is much larger than those of refueling tests and US diurnal tests with Euro 4 vehicles. The SOAP using comprehensive profiles is much higher than that given using headspace vapors, especially in winter (7.2 times higher in December). So, using headspace vapor to represent

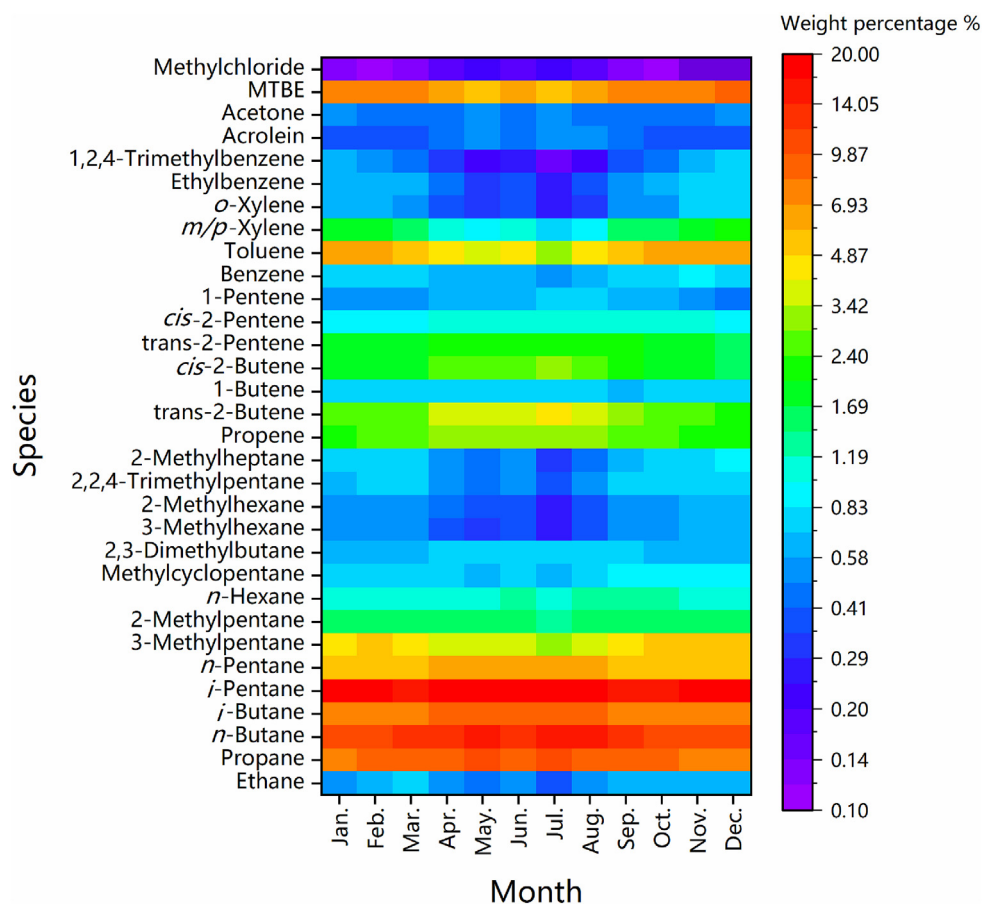


Fig. 7. The comprehensive species profile of evaporative emissions of the different month in Beijing.

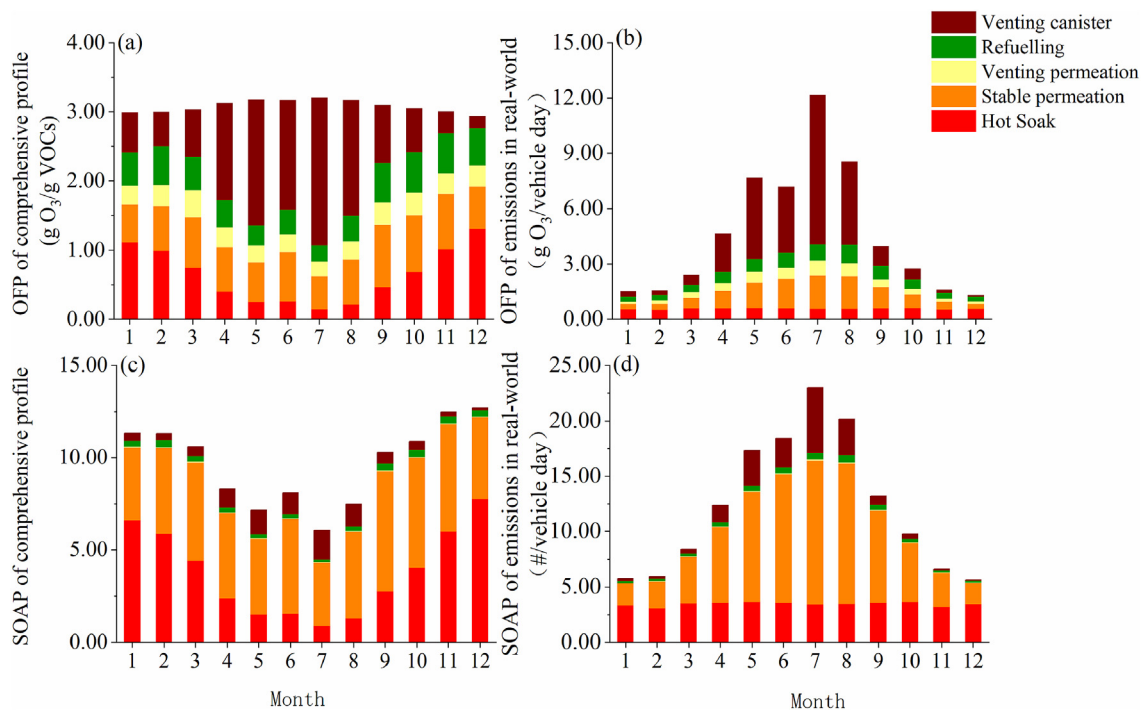


Fig. 8. Monthly OFP (a) and SOAP (c) of the comprehensive species profile in Beijing. OFP (b) and SOAP (d) of evaporative emissions from one vehicle per day in different months.



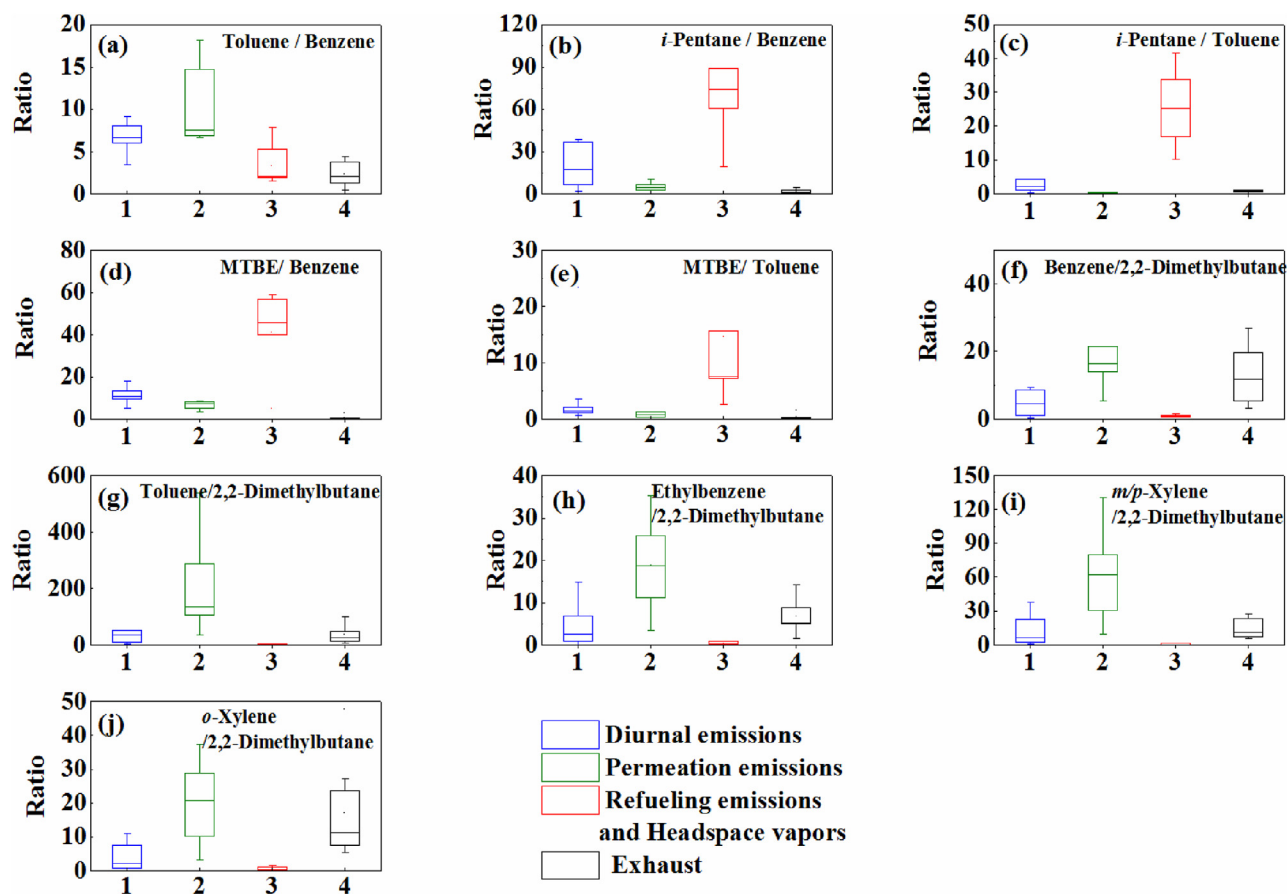


Fig. 9. The weight percentage ratios among toluene, benzene, ethylbenzene, xylenes, 2,2-dimethyl butane, and MTBE.

evaporation leads to an underestimation of the contribution of evaporation to SOA yield significantly, especially in winter.

### 3.4. Indicators to distinguish evaporative VOCs emissions from exhaust VOCs emissions

We further evaluate the species or indicators that could be used as indicators of vehicular evaporative VOCs emissions. Toluene, benzene, ethylbenzene, and xylenes are typically used as indicators for vehicle-related emissions [22,25,26,40,41,44–47]. These components were observed in both the tailpipe exhaust and evaporative emissions, implying that none of the single components could be used as a tracer to distinguish evaporation emissions from exhaust emissions. In this work, we test the possibility of using the ratios among these typical VOCs species to distinguish exhaust and evaporation. As shown in Fig. 9, the ratios of toluene/benzene, *i*-pentane/benzene, *i*-pentane/toluene, benzene/2,2-dimethylbutane, toluene/2,2-dimethylbutane, ethylbenzene/2,2-dimethylbutane, and xylenes/2,2-dimethylbutane have overlaps for tailpipe emissions and evaporative emissions from different processes. Hence, these ratios cannot be used as indicators for either tailpipe or evaporative emissions. For all research data, the ratios of MTBE/benzene and MTBE/toluene were extremely low from exhaust VOCs emissions, thus can serve as indicators for evaporation. Besides, when venting dominates VOCs emissions, MTBE/benzene and MTBE/toluene ratios are in the range of 18.7–58.3 and 2.3–23.7, respectively, much higher than the permeation dominated emissions (i.e., 5.3–10.3 and 0.7–1.6, respectively). Thus, these two ratios can further distinguish emission mechanisms for evaporation.

## 4. Conclusion

In this study, we analyze the VOCs speciation profiles of vehicular evaporations for different test processes, emission processes, and temporal changes in the real-world. Though butane and pentane are the major species for all evaporative emission processes, the species from different emission processes differ significantly. The contributions of the two main mechanisms (permeation and venting) lead to different VOCs speciation in different diurnal test processes. Furthermore, detailed species profiles of emission processes were summarized by measured species in refueling tests, hot soak tests, static permeation tests, and calculated profiles based on mass balance during diurnal tests. We find that traditional headspace vapors cannot represent the whole of the evaporation processes. Using species profiles of headspace vapors represent evaporative emissions could only reflect parameters of refueling emission from vehicles without ORVR. When the new standard implied, this would not work anymore.

Comparing the comprehensive VOCs speciation profile to the profile of headspace vapors, aromatics changed from 5.80% to 13.28%, 5 to 12 times higher than headspace vapors. The impact of vehicle evaporative emissions on ozone formation in July would be 8 times higher than that in January. For SOAP, 100 g of evaporative emissions are equal to 6.05–12.71 g toluene in different months. The SOAP using comprehensive profiles is much higher than that given using headspace vapors, especially in winter (7.2 times higher in December). These findings would improve our understanding of the evaporative VOCs emissions in China and their environmental impacts (e.g., O<sub>3</sub> and SOA formation).

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ese.2019.100002>.

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