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Source apportionment of volatile organic compounds (VOCs) in vehicle cabins diffusing from interior materials. Part I: Measurements of VOCs in new cars in China

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ABSTRACT

Vehicle air quality is a topic of interest but information regarding the composition and sources of interior volatile organic compounds (VOCs) is incomplete. This study improves this situation by determining VOC species that deserve to be concerned in new vehicles and providing basic data for source apportionment. VOC measurements in 86 vehicles manufactured between 2017 and 2018 from 10 of the top-selling models in the Chinese market were performed. A total of 41 species were identified as "noteworthy" VOCs in new vehicles based on five criteria: prevalence, possible health effects, possible odors, characteristic presence in vehicles, and high concentrations. Significant correlations were found for approximately half the 820 [(41 × 40)/2] possible pair combinations of the 41 determined VOCs suggesting they come from a few common sources. The data could improve our understanding of VOC levels in new vehicles and can be used for source apportionment.

1. Introduction

People spend considerable time in automobiles traveling for work, shopping, and recreational activities [1–3] and vehicle cabins are an important part of the indoor environment. Vehicle cabins are a microenvironment with a relatively small volume exposed to possible emissions from a variety of materials including seats, carpets, ceiling materials, doors, and adhesives [4–8]. Pollutants such as volatile organic compounds (VOCs) can accumulate in the confined space and have negative impacts on the air quality of vehicle cabins.

Air pollution in vehicle cabins reflects the combined contributions from many sources including from ambient air, vehicle exhaust, chemical reactions inside the cabin, human occupants, and interior materials [9–13]. VOCs from interior materials make an important contribution, especially for new vehicles and when vehicles are parked with doors and windows closed. The automotive industry is in a period of rapid change with new materials and manufacturing processes being introduced. The current understanding about which interior materials are the main emission sources and their contributions to interior pollutant concentrations is however insufficient. Therefore, studies of source apportionment in vehicle cabins by VOCs diffusing from interior materials are needed. To that end, knowing which VOCs are mainly emitted from interior materials is an important first step.

The literature for measurements of air quality inside vehicle cabins has been reviewed and a brief summary is given below. Yoshida et al. measured the VOC concentrations in 101 parked and closed vehicles produced in Japan in a low density traffic [14]. A total of 159 VOCs were detected and their concentration ranges were provided. Xu et al. investigated concentration levels of eight compounds in seven used vehicles (approximately 5-year usage) and eight newer ones (less than 1-year usage) under driving conditions [9]. A field test in three vehicles by You et al. was performed in an environmental chamber, and concentrations of the top 20 compounds in each car were reported [15]. These studies have provided a basic understanding of chemicals inside vehicles, but the investigated samples were used vehicles. The obtained VOC species may attribute to the combined contributions of interior materials, ambient air, and emission sources introduced by users. Noteworthy VOCs in vehicle cabins emitted from interior materials need to be further studied.

The studies regarding air quality surveys in new vehicles have also been reviewed. A field test of 802 new vehicles was performed by Zhang et al. in an underground parking garage with average concentrations of four target compounds reported [16]. Joanna et al. identified 18 target chemicals and 10 main hydrocarbons in vehicle interiors from air

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samples in five new vehicles [17]. Chien investigated the levels of 12 target VOCs in five new cars [18]. In these studies, only a few specific VOCs were focused, information on other compounds, however, was not provided. In comparison, a few investigations have been performed on detail description of detected VOCs. Yoshida and Matsunaga determined as many as 161 organic compounds in one private car [19]. Brodzik et al. surveyed air composition in nine new vehicles of the same model, and quantitative concentrations of 81 VOCs were provided [20]. Faber et al. investigated 64 commonly detected VOCs in nine vehicles of the same model [21]. These studies have the advantage of comprehensive data description, but the number of vehicles tested was relatively limited. Besides, the investigated samples were produced in either Japan or Poland, detail information of air quality in vehicles manufactured in other regions such as China was insufficient.

The aim of the present study was to investigate the current situation of overall VOC species and concentration levels, mainly diffused from interior materials, in vehicle cabins, and further to provide the noteworthy compounds and basic data for source apportionment. To achieve this, 86 new private-use vehicles manufactured between 2017 and 2018 from 10 of the top-selling models in the Chinese market were randomly selected for investigation. The VOC species and concentration levels in these samples were surveyed in field tests. Based on a consideration of prevalence, possible health risks, possible odors, characteristic nature, and high concentrations, "noteworthy" compounds from 6 to 12 carbons in new private-use vehicles were determined and the results were then compared with those in the literature. Correlations among the determined VOCs were analyzed using Spearman's Rank Order test. Results of source apportionment will be provided in the companion paper.

2. Materials and methods

To assess the in-vehicle VOC composition emitted from interior materials, experiments should be designed to avoid the possible influences of pollutants introduced during the use phase and the sampling process. In terms of the former, it could be avoided by the appropriate sample selections. As for the later, a rigorous sampling procedure could become the solution. After collecting the air samples in vehicle cabins, the qualitative VOC compositions and their quantitative concentration levels become the next important question, which could be determined by the accurate air sample analysis and quality assurance processes.

2.1. Tested vehicles

The new vehicle is the focus of this study because the VOCs' presence inside is mostly connected with interior material emissions. A survey of the sales of different vehicle models in the Chinese market was performed, and 10 top-selling models in 2017 were chosen for investigation. The minimum sample size for the study was determined using the formula [22]:

$$N = \frac{Z^2 \times (P \times (1 - P))}{E^2} \tag{1}$$

Where N is the sample size, Z is the statistical value of the corresponding confidence interval, P is the degree of sample variation, and E is the error range.

Considering the balance between study cost and statistical robustness, a confidence interval of 90% ($Z = 1.64$), a sample variation degree of 0.5 ($P = 0.5$), an error range of 10% ($E = 10\%$) were selected. Therefore, a sample size of no less than 67 vehicles was required according to equation (1). As a contingency against potential experimental problems in the field, more vehicles were investigated than the minimum design sample size of 67, and experiments were performed using a total of 86 vehicles with 8–10 samples for each model. With the information on vehicle model and sample size, the new vehicles manufactured between 2017 and 2018 were randomly selected from various car dealers.

2.2. In-vehicle air sampling

Depending on the purpose of research, air samples in either parked or driving vehicles could be collected. Considering the main aim of this study, the air sampling in the former situation was adopted, because VOCs emitted from interior materials will be most evident when the vehicles are parked with doors and windows closed. We note that compared with the driving situation, measuring air quality in a parked sealed vehicle is the worst case for human exposure in a vehicle cabin.

Normally, to collect air samples from vehicles under such a condition, two processes are needed [9,14–21,23] including: (1) The cars are maintained at closed conditions for a certain period; (2) The air samples are collected from vehicle cabins. For the former, the observed closing time varied from 20 min to 16 h. In the case of latter, although Tenax TA adsorption tubes were uniformly used to collect interior air, different sampling positions were adopted including in-vehicle or out-vehicle. As these operations have influences on measurement results, they should be well taken into account prior to sampling. In addition, a procedure was added to reduce the possible influence of initial in-vehicle background pollutants. Therefore, a total of three processes were performed: (1) Reduce background pollutants; (2) Keep closed conditions; (3) Collect air samples.

For the first process, the selected vehicles were required to park at a well-ventilated outdoor parking lot prior to sampling, following the general parking habits of the Chinese consumers. There were no potential sources nearby such as gasoline stations or chemical plants, aimed to eliminate the influence of outdoor pollutants on in-vehicle air quality. Then, the engine and air conditioner were turned off. Thereafter, all the windows and doors were maintained open to reduce background VOCs in the cabin. The natural ventilation time was suggested by a concentration decay test, which showed the interior total VOC concentration reached a comparable level of ambient air when opening for 30 min, using the ppbRAE 3000 (PGM-7340, RAE Systems Inc, USA) with a detection range from 1 ppb to 10000 ppm and test resolution of 1 ppb. Therefore, a natural ventilation time of no less than 30 min was required for each vehicle.

After reducing the background pollutants, the vehicles were maintained at closed conditions for a certain time before air sampling. A large range of the closing time in previous literature was observed, varied from 20 min to 16 h, and no unified time could be referred. As the closing time has an influence on both detected VOC species and their concentrations, and it was thus examined in advance by a preliminary experiment in this study. The increasing trend of total VOC concentration in a vehicle, sharing the same closing conditions with the selected samples, was monitored by the ppbRAE 3000. The interior concentration was observed to reach a relatively steady state after 6 h closing, with the concentration change of no more than 5% afterward. Thus, we determined that closing time of no less than 6 h was needed prior to air collecting.

Interior air samples were collected outside the vehicle to reduce the possible influences of door opening. A Teflon tube, used as the sampling line, was installed as shown in Fig. 1. One end of the tube was placed in the middle of the front two headrests at the height of the human breathing zone. The tube was led outdoors from the upper corner of the vehicle's door, without destroying the airtightness. Before air collection, the residual air inside the sampling tube was removed by a sampling pump (QC-II, Beijing Municipal Institute of Labor Protection, China), eliminating the influence of non-interior VOCs on measurement results. Thereafter, interior air was collected at the outlet of Teflon tube through a Tenax TA tubes (Markes, UK), using the sampling pump. The pump was operated at a flow rate of 200 mL/min for 30 min, and 6 L of air was sampled. The Tenax absorption tube samples were sealed with aluminum foil and stored in a low-temperature environment (approximately 4 °C) prior to analysis.

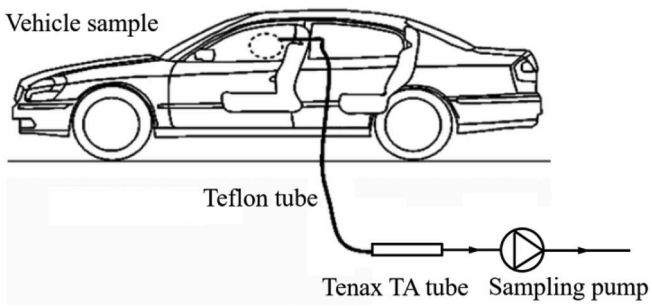

Fig. 1. Schematic of in-vehicle air sampling.

Considering that temperature may have a great influence on material emissions, air samplings were performed in four seasons so that the overall in-vehicle VOC concentration ranges all year round could be revealed as much as possible. Besides, approximately half samples were investigated in summer because in-vehicle air quality problem tends to be more serious at high temperatures. During the measurement, an automatic sensor and data logger (WSZY-1, Beijing, China) with the precision of 0.1 °C was placed near the interior sampling point to monitor the temperature continuously. The temperature distributions inside the test vehicles are shown in Table 1. Interior temperature for all the investigated samples varied from −13.1 °C to 50.3 °C with an average value of 32.6 °C.

2.3. Air sample analysis

The identification of VOCs in the Tenax TA tubes was performed by TD-GC/MS. The Tenax TA tubes were placed in a thermal desorber (TD; Markes, UK), including a two-stage unit in which the tube desorption was maintained at a temperature of 250 °C for 10 min and the internal trap desorption at 300 °C for 3 min. Nitrogen was used as a carrier gas during the desorption process, with a flow rate of 55 mL/min. The desorbed compounds were then separated on an HP-VOC capillary column (60.0 m × 200 μm × 1.1 μm film thickness, Agilent, USA) using helium carrier gas with a flow rate of 1 mL/min. The split ratio of analytes introduced into the chromatographic column was 1:30. The initial oven temperature was set at 40 °C for 3 min, ramped to 230 °C at 10 °C/min, and then maintained at 230 °C for 3 min. The ion source and quadrupole rod were maintained at 230 °C and 150 °C, respectively. The mass spectrometer was operated to scan the entire range ($30 \leq m/z \leq 300$) in the total ion scan mode, with a frequency of 2.5 Hz. VOCs were confirmed by retention time compared with that obtained for standard compounds from Institute for Reference Materials, Chinese Ministry of Environmental Protection, China and mass spectra (NIST standard library). The chemicals with scores above 80% were considered to have the acceptable quality of fit and regarded as identified compounds [18].

2.4. Quality assurance

VOCs were quantified using an external standard calibration. Standard solutions containing benzene, toluene, ethylbenzene, p-xylene, m-xylene, o-xylene, styrene, butylacetate, and undecane were purchased from the Institute for Reference Materials, Chinese Ministry of Environmental Protection with concentration levels of 10 mg/L and 100 mg/L. Standard solutions with eight different contents (20 ng, 50 ng, 80 ng, 100 ng, 200 ng, 500 ng, 800 ng, and 1000 ng) were injected into eight Tenax TA tubes. The tubes were then thermally desorbed using the same procedure as for the samples. By fitting the eight concentration points, calibration curves were obtained, with $R^2 > 0.99$ for all quantified VOCs. Quantification of the nine compounds was achieved using the corresponding calibration curves, while other VOCs were calculated as toluene equivalents [12]. The detection limit was approximately 1 ng for each compound, which was determined by the ratio of signal-to-noise (S/N = 3/1).

Duplicate samples were taken from half of the investigated vehicles to examine the reproducibility of the results. The average relative standard deviations (RSD) were within 15% for the duplicate samples, indicating good reproducibility for the interior concentrations. In addition, field blank analyses (RSD<5%) were taken periodically. Laboratory blanks and pump calibrations by a soap film flowmeter (Mini-BUCK M-5, USA) were performed prior to air sampling. Instrument errors from the GC/MS and the sampling procedure were controlled by routine operational maintenance and standard sample calibrations.

Table 1
Temperature distributions inside the test vehicles.

In-vehicle temperature range (°C)	Total number for the range
[-20,-10)	4
[-10,0)	4
[0,10)	5
[10,20)	5
[20,30)	8
[30,40)	41
[40,50)	18
[50,60]	1

3. Results and analysis

3.1. VOC species with high detection rate in vehicles

More than 200 VOC species were identified by TD-GC/MS in the 86 vehicles. The frequency of a VOC being detected in the samples was used for the basic selection of measurement data. Compounds detected in more than 50% of the samples were considered as "common" and deserving further consideration [18]. Following such a data selection principle, a total of 52 VOCs detected in more than 50% of the samples were identified.

These compounds were categorized into four groups on the basis of their chemical structure: aliphatic compounds, carbonyl compounds, aromatic compounds, and others. The number distribution of these compounds is shown in Fig. 2. Aliphatic compounds were the most abundant group, accounting for 17 (32.7%) of the 52 VOCs detected and were further classified into alkanes, cycloalkanes, and alkenes. There were 12 alkanes, 3 cycloalkanes, and 2 alkenes. Aromatic compounds and carbonyl compounds were the same, both accounting for 10 (19.2%) of total numbers. Among carbonyl compounds, half were ketones and others were aldehydes. Compounds lumped together as "others" in Fig. 2 included esters, alcohols, and halocarbons and numbered 15 compounds. Aliphatic, carbonyl, and aromatic compounds together accounted for 37 (71%) of the 52 common VOCs observed in new vehicles.

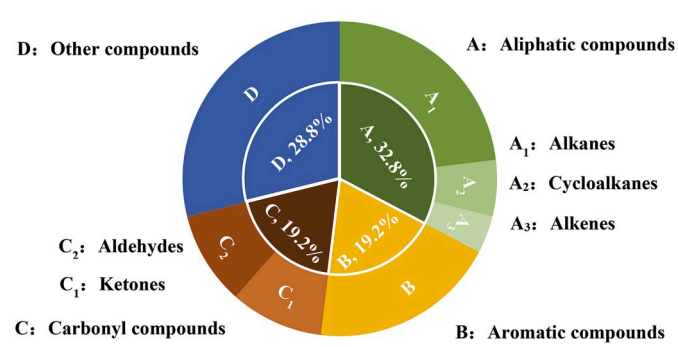

Fig. 2. Number distributions of common VOCs in the 86 new vehicles tested.

3.2. Noteworthy VOC species in vehicle cabin air

Although the primary selection for measurement data was performed, the single parameter of detection rate was not enough to determine which compounds were concerned in the cabin since the influences of VOCs on in-vehicle air quality were not considered. Further analysis of the detected VOCs was conducted based on their possible health risks, odors, characteristic nature, and concentrations, in decreased order of importance.

3.2.1. VOCs with possible health risks

The potential influence of vehicle air quality on human health is a primary motivation for research in this area. To screen for such VOCs, the classifications from the International Agency for Research on Cancer (IARC) were used. IARC classifies carcinogenic agents into the following groups: Group 1 (carcinogenic to humans), Group 2A (probably carcinogenic to humans), Group 2B (possibly carcinogenic to humans), Group 3 (not classifiable in terms of its carcinogenicity to humans), and Group 4 (probably not carcinogenic to humans) [24]. Usually, VOCs in Groups 1, 2A, 2B, and 3 are considered to have possible health risks and command attention [25].

VOCs detected in more than 50% of the vehicles were compared with those in these groups proposed by IARC, and 13 compounds with possible health risks were identified as shown in Fig. 3. Most of the compounds belong to group 2B and 3. Benzene and 1,2-dichloropropane were the only Group 1 compounds and styrene was the only Group 2A compound detected. From the perspective of chemical structure, aromatic compounds are clearly over-represented in Fig. 3 and deserve attention in assessments of the potential health effects of in-vehicle VOCs. In terms of quantitative results, the concentrations of most compounds in Fig. 3 ranged from ND (concentration lower than the detection limit) to 100 μg/m^3. However, some VOCs such as toluene (1.43–425 μg/m^3), xylene (ND-345 μg/m^3), styrene (ND-262 μg/m^3), and ethylbenzene (ND-143 μg/m^3) had much wider concentration distributions. As seen from Fig. 3, of the 13 compounds classified by IARC, toluene had the widest concentration range and highest average concentration (53.1 μg/m^3) in vehicle samples. Moreover, it was detected in all the measured vehicles.

3.2.2. VOCs which may contribute to odors

Complaints of unpleasant odors in vehicle cabins are a serious issue for vehicle manufacturers. Thus VOCs that can lead to unpleasant odors in vehicle cabins deserve attention. Research has shown that the generation of VOC odors may be related to its functional group and molecular size [26]. Acids and carbonyl compounds especially with small molecular size may have noticeable odors [27–29]. Among the VOCs with high detection rates in measured vehicles, six fall into this category: hexanal, heptanal, benzaldehyde, nonanal, acetophenone, and acetic acid. In addition, ethylacetate, butylacetate, and butanol have been shown to cause an olfactory response under certain circumstances [30–32]. Therefore, the above-mentioned nine VOCs were included in our list of noteworthy compounds in vehicle cabins because of their possible contribution to odors.

The concentration distributions of these VOCs in measured vehicles are shown in Fig. 4. Ethylacetate (ND-277 μg/m^3), nonanal (ND-182 μg/m^3), butylacetate (ND-155 μg/m^3), and butanol (ND-115 μg/m^3) had the largest concentration distributions, while others ranged from ND to approximately 50 μg/m^3. Although there were large differences in the ranges of concentration observed for the different VOCs in Fig. 4, their average concentrations were comparable from 4.61 μg/m^3 to 16.0 μg/m^3 except for heptanal, which has the lowest value of 1.96 μg/m^3.

It should be noted that although nine VOCs were detected that could lead to odor problems, conclusions regarding whether these compounds actually cause an unpleasant odor in the measured vehicle cabins should not be drawn. The perception of VOC odors is extremely complicated, influenced by olfactory thresholds and subjective feelings of humans, and beyond the scope of the present work.

3.2.3. VOCs characteristic of vehicle cabins

Although the vehicle cabin can be considered as an indoor environment in a broad sense, there are important differences in interior air quality between vehicle cabins and other typical indoor environments, such as residences. These differences are related to the characteristic VOCs in the vehicles. The determination of these characteristic compounds is helpful in understanding the specific environment in vehicle cabins. Identifying VOCs which are abundant in vehicles but are rare or absent in other indoor environments provides a path to understanding the unique features of in-cabin VOC sources.

To screen for such compounds, the main VOC components in vehicles were compared to those in other typical indoor environments. Normally, the residence is considered as one of the most typical and important indoor environments, because of the long-time people spend at home. The literature regarding air quality in residential buildings was reviewed. A total of eight representative studies were compared, containing VOC field survey results from 3881 residences in 7 different countries around the world [33–40]. These studies provide VOC compositions and concentration distributions, in the investigated residences, and the reported VOCs numbers ranged from 8 to 193, with an average of 54 VOCs in each study. Considering the detailed data analysis and the

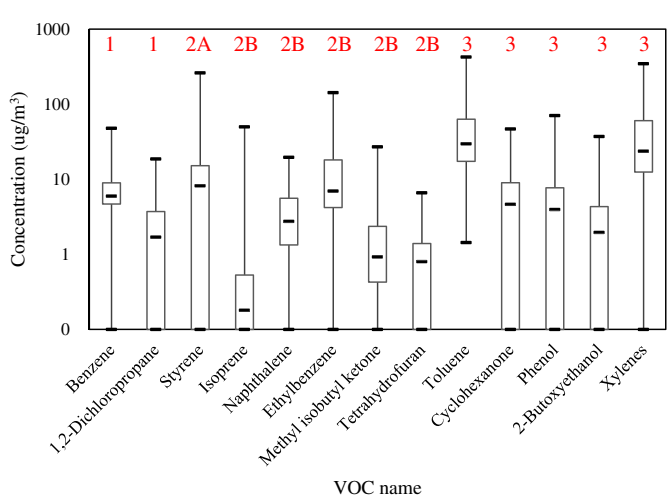

Fig. 3. Concentration distributions of VOCs with possible health risks in vehicles. The IARC hazard classification groups (1, 2A, 2B, 3) are given.

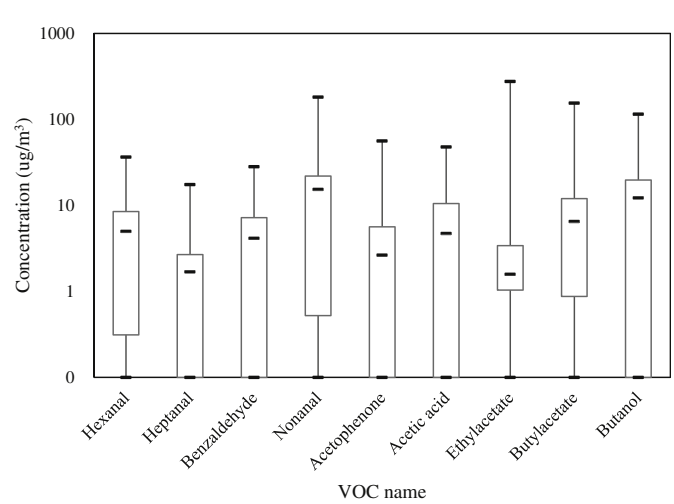

Fig. 4. Concentration distributions of VOCs that could cause odor in vehicles.

large sample size in multiple regions around the world, the VOC species provided in these studies could represent the main compounds in residences.

Comparing the main VOC species in vehicles with those in residences, three types of comparison results could be obtained. The first type included VOCs that were abundant in residences but not found in vehicles, such as the limonene and α-pinene. These compounds were out of scope in this study. The second type involved VOCs that were commonly observed in both environments, such as the toluene and benzene, indicating their diverse sources. For the last type, the VOCs were rich in vehicles but hardly observed in residences, which could be deemed the characteristic VOCs in vehicle cabins. A total of eight such compounds were screened out, namely 2,2,4,6,6-pentamethylheptane, oxime-2-butanone, 1-methyl-2-ethylbenzene, trimethylsilanol, N,N-dimethylformamide, hexamethylcyclotrisiloxane, 2-ethyl-1-hexanol, and octamethylcyclotetrasiloxane. Of these compounds, the former six were not detected in residences, and the other two were reported in just one study indicating their presence in residences was possibly related to the investigated samples rather than a general conclusion. Consequently, they could still be deemed characteristic VOCs in vehicles, different from those in residences.

Concentration distributions of characteristic VOCs in the measured vehicles are shown in Fig. 5. Obviously, 2,2,4,6,6-pentamethylheptane was observed to have the largest concentration range (ND-493 μg/m^3), which were far larger than those of others ranged from ND to less than 200 μg/m^3. In terms of average concentration, similar conclusions were observed. 2,2,4,6,6-Pentamethylheptane was detected with the highest average concentration of 47.1 μg/m^3. The other six compounds, trimethylsilanol, 1-methyl-2-ethylbenzene, N,N-dimethylformamide, octamethylcyclotetrasiloxane, hexamethylcyclotrisiloxane, and 2-ethyl-1-hexanol, had a comparable level from 5.50 μg/m^3 to 25.1 μg/m^3, while oxime-2-butanone had the lowest average concentration of 0.93 μg/m^3.

3.2.4. VOCs with high concentrations

In addition to VOCs that possible have health risks, odors, and are characteristic for the vehicle environment, compounds present at high concentrations in vehicle cabins also deserve attention. Aliphatic and aromatic compounds make a large contribution to interior VOC concentrations [14]. The following commonly observed aliphatic and aromatic compounds in the present study were added to our list of noteworthy VOCs: pentane, hexane, heptane, 4-methyloctane, 2,4-dimethylheptane, 3-methylnonane, undecane, dodecane, cyclohexane, 1,2,3-trimethylbenzene, and 1,2,4-trimethylbenzene.

The concentration distributions of these VOCs are shown in Fig. 6. The small linear aliphatic compounds from pentane to 2,4-dimethylheptane were observed at concentrations in the range ND-100 μg/m^3. The maximum concentration of the large linear aliphatic compounds 3-methylnonane, undecane, and dodecane were higher and ranging from 163 μg/m^3 to 231 μg/m^3. Cyclohexane had a concentration range from ND to 29.6 μg/m^3, which was smaller than the linear aliphatic compounds excluding the heptane. The concentration of the two aromatic compounds, 1,2,3-trimethylbenzene and 1,2,4-trimethylbenzene, ranged from ND to 361 μg/m^3, which were larger than that of most aliphatic compounds. As seen in Fig. 6, although there were large differences in the range of concentrations observed for the different VOCs, the mean concentrations were comparable and ranged from 4.0 μg/m^3 to 24.3 μg/m^3. All of the VOCs in Fig. 6 were found in over 70% of the measured samples, indicating they were abundant in new vehicles.

Based on a consideration of prevalence, possible health risks, possible odors, characteristic nature, and high concentrations, totally 41 compounds were identified as noteworthy VOCs from 6 to 12 carbons in the vehicle cabins in new vehicles. The statistical profile of concentration distributions of these compounds is listed in Table S1, described by the values of minimum, 1st quartile (25%), median (50%), 3rd quartile (75%), maximum, and mean.

3.3. Comparison with the literature

The results in Table S1 were compared with those in the literature. The research presented by Brodzik et al. [20] and Faber et al. [21] attracted primary attention, because of the investigation on new vehicles along with comprehensive descriptions of detected VOC concentration distributions. However, the vehicle doors were open to allow the entrance of air collectors prior to sampling in both studies, which were different from the air collection processes in this paper. The different operations may lead to different investigation results. Therefore, the results in Table S1 may not be directly comparable to those in both papers. As for the new vehicle air quality survey results in other literature [9,15,16], only a few VOC species were focused and most of the compounds in Table S1 were not provided in those studies. Thus, field investigations of in-vehicle VOC species in used vehicles were

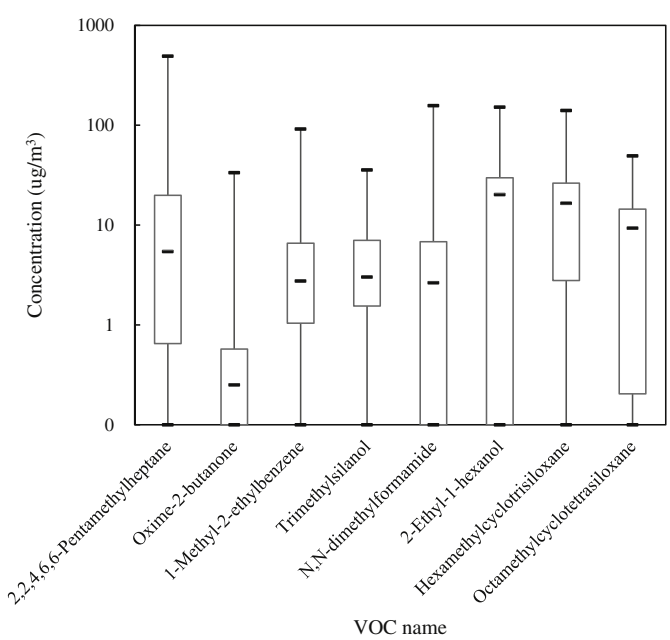

Fig. 5. Concentration distributions of characteristic VOCs in vehicles.

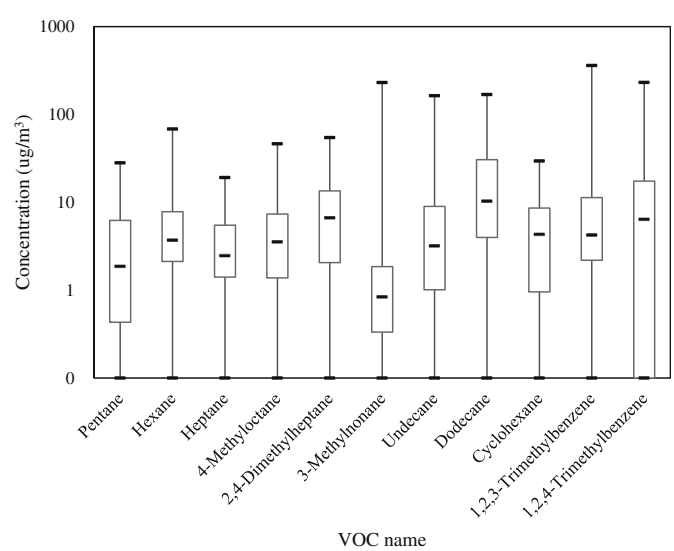

Fig. 6. Concentration distributions of VOCs with high concentrations in vehicles.

compared. It was found that the study by Yoshida et al. [14] achieved prominent results on both numbers of measured sample size and comprehensive description of detected compounds, and was thus taken for comparison. The differences between the two studies were thus discussed from two aspects, namely qualitative VOC compositions and quantitative concentration distributions. The results are displayed in Table 2.

As seen in Table 2, most of the VOC species identified in the present work were detected by Yoshida et al. [14]. Eight VOCs with the label "-" in Table 2 were not mentioned in the literature. Among these compounds, three of them, namely isoprene, acetic acid, and pentane, were not in the concerned VOC list by Yoshida et al. [14] who focused the chemicals from 2-methylpentane up to tricresyl phosphate. While the other five were not detected in the literature, and the reasons were analyzed as follows. The detection of 2,2,4,6,6-pentamethylheptane, oxime-2-butanone, hexamethylcyclotrisiloxane, and octamethylcyclotetrasiloxane in the present work is probably related to emissions from adhesives used in vehicles [41–43]. With the development of vehicle manufacturing technology, welding is being replaced by bonding during the vehicle assembly process to reduce the weight of the vehicle body and consequently decrease fuel consumption. To support the smooth implementation of such a method, various adhesives are widely used in vehicle cabins. Therefore, more VOCs related to adhesive emissions could be found in the measured samples. These findings may support the conclusion that the VOC compositions in the current vehicles may be different from those manufactured in 2001–2004 which were surveyed by Yoshida et al. [14]. Trimethylsilanol is produced from the hydrolysis of polydimethylsiloxane, employed as the moisture-repellent to improve the hydrophobicity, flexibility, and comfort of leather seats [44,45]. Normally, the chemical reaction rate is faster at the initial time, and it will gradually decrease or even disappear over time [46]. The investigated samples were new vehicles in this study, while those in the study by Yoshida et al. were used ones. This may lead to the phenomenon that more trimethylsilanol was detected herein.

Table 2
Comparisons of results with those from Yoshida et al. [14].

VOC name	Concentration ranges (μg/m^3)	
	This study	Yoshida et al. [14]
I: Possible health risks		
Benzene	(ND-47.9)	(0.88–33)
1,2-Dichloropropane	ND-18.7)	*
Styrene	(ND-262)	(0.09–79)
Isoprene	(ND-50.0)	–
Naphthalene	(ND-19.6)	(0.27–7.3)
Ethylbenzene	(ND-143)	(2.2–59)
Methylisobutylketone	(ND-148)	(0.61–266)
Tetrahydrofuran	(ND-6.60)	(0.35–23)
Toluene	(1.43–425)	(12-356)
Cyclohexanone	(ND-46.7)	(0-23)
Phenol	(ND-70.6)	–
2-Butoxyethanol	(ND-37.1)	(0.32–30)
Xylene	(ND-346)	(4.6–90)
II: Possible odors		
Hexanal	(ND-36.6)	*
Heptanal	(ND-17.5)	*
Benzaldehyde	(ND-28.2)	*
Nonanal	(ND-182)	(2.1–20)
Acetophenone	(ND-56.2)	(0.24–5.8)
Acetic acid	(ND-47.8)	–
Ethylacetate	(ND-277)	(0.98–84)
Butylacetate	(ND-155)	(0.32–30)
Butanol	(ND-115)	(2.2–538)
III: Characteristic VOCs		
2,2,4,6,6-Pentamethylheptane	(ND-493)	–
Oxime-2-butanone	(ND-33.5)	–
1-Methyl-2-ethylbenzene	(ND-91.7)	(0.51–29)
Trimethylsilanol	(ND-35.7)	–
N,N-dimethylformamide	(ND-157)	*
2-Ethyl-1-hexanol	(ND-152)	(0.51–11)
Hexamethylcyclotrisiloxane	(ND-141)	–
Octamethylcyclotetrasiloxane	(ND-49.4)	–
IV: High concentration VOCs		
Pentane	(ND-28.2)	–
Hexane	(ND-68.4)	(3.4–186)
Heptane	(ND-19.2)	(1.6–374)
4-Methyloctane	(ND-46.4)	(0.27–22)
2,4-Dimethylheptane	(ND-54.6)	(2.2–402)
3-Methylnonane	(ND-231)	(0-47)
Undecane	(ND-163)	(1.3–185)
Dodecane	(ND-169)	(1.4–179)
Cyclohexane	(ND-29.6)	(0.80–194)
1,2,3-Trimethylbenzene	(ND-361)	(0.42–25)
1,2,4-Trimethylbenzene	(ND-232)	(2.0–98)

"ND": The concentrations of these compounds were lower than the detection limit.
"-": Not mentioned by Yoshida et al. [14].
"*": Detected but concentrations not reported.

Some VOCs reported in the literature were detected herein, including p-dichlorobenzene, limonene, β-linalool, dihydromyrcenol, and nicotine. p-Dichlorobenzene was widely used as a fumigant and insecticide for mildew, mold, and moth control [14] and has been commonly observed in residential buildings [47]. The presence of limonene, β-linalool, and dihydromyrcenol is related to their use as air fresheners and they were not detected in cabins where air fresheners were not used. Nicotine was a major compound in tobacco smoke and was rich in the vehicle cabins where occupants usually smoked [48]. The detection of these compounds shows that VOC compositions in used vehicles are different from those in new ones, and chemicals introduced during the use phase should be separated from the vehicles themselves.

In terms of quantitative concentrations, the only parameter provided in the reference was the concentration range, and this was thus taken for comparison. Among the compounds, five marked by "*" in Table 2 were not provided with quantitative concentrations in the literature. As for other VOCs, the minimum detected concentrations in this study were below the detection limit except for the toluene, and most of these values were lower than those in the literature. The possible reason was that diverse vehicle models were investigated in this study. The previous study has proved that large variations of detected VOCs existed among different models [49]. This will lead to the phenomenon that the same VOC was hard to be found in all the measured samples, and the minimum concentration was thus below the detection limit. When comparing the maximum detected concentration, such a value was in the same order of magnitude for most compounds between the two studies. While it was obvious that the differences were larger for the 2-ethyl-1-hexanol and heptane. This probably reflects the effects of the emission strength of interior materials.

The in-vehicle VOC concentration levels in the present work were also compared with the literature in the past to explore the VOC concentration trends for new vehicles over time. A field investigation was performed by Zhang et al. [16] in a well-ventilated underground parking garage to estimate the pollutant level in 802 new vehicles manufactured in approximately 2003. The investigated samples in that work were also the vehicles sold in the Chinese market. Average concentrations of the focused VOCs from Zhang et al. [16] were compared, namely benzene, toluene, and xylene, and the results are shown in Table 3.

Intuitively, concentration levels of the three compared VOCs in new vehicles all exhibited a noticeable decay pattern over time. Benzene was observed to have the largest decrease, followed by toluene. Concentrations of the two compounds in the current new cars were approximately

Table 3
Comparisons of results with those from Zhang et al. [16].

VOC name	Average concentration (μg/m^3)	
	This study	Zhang et al. [17]
Benzene	8.75	270
Toluene	53.1	1220
Xylene	47.0	170

1/30 and 1/20 of those in the new vehicles manufactured 15 years ago. The decay rate for the xylene was relatively small compared with the other two compounds, even so its concentration was still about 1/4 of that in the new vehicles measured by Zhang et al. [16]. These findings suggest the improvement of air quality in the new vehicle as time went by. Such a change may be related to the promulgation of in-vehicle air quality standards in 2011 named "Guideline for Air Quality Assessment of Passenger Cars" [50]. Due to constraints of the standard, more low off-gassing materials were used to reduce the in-vehicle pollutant levels. The comparison results indicated the effectiveness of such a move on the elevation of in-vehicle air quality.

3.4. Correlation analysis among the noteworthy VOCs

As a preparation of VOC source apportionment in vehicle cabins, correlation analysis among the 41 noteworthy VOCs was conducted using Spearman's Rank Order correlation test method. Concentrations of VOCs that were below the detection limit were substituted with one-half the method detection limit. The test showed positive correlations among the 41 VOCs. Of the 820 [(41 × 40)/2] possible pair correlations, 108 (13.2%) had p-values > 0.05, 180 had p-values between 0.05 and 0.001, 125 had p-values between 0.001 and 0.000061, and 407 (407 = 820-108-180-125) had p-values < 0.000061 (see Table S2). Based on the Bonferroni correction method, the correlation was considered to be statistically significant if the p-value is less than alpha (0.05) divided by the number of hypothesis tests. The value of 0.000061 corresponds to 0.05 divided by the 820 [(41 × 40)/2] tests. It should be mentioned the obtained correlation result by Bonferroni correction method is much stricter than that by others. Even so, approximately half of the Spearman rank order correlation results were statistically significant, indicating the compounds with strong correlations probably come from a few common sources or at least their composition was similar in the measured vehicles. This finding provided significant information for the VOC source apportionment in vehicle cabins.

This paper is mainly focused on determining the noteworthy VOC species and quantitative concentration levels in vehicle cabins, based on field air sampling and GC/MS analysis. Statistical correlation analysis was performed to explore the VOCs that come from a few common sources. Quantitative analysis and discussion regarding the main emission sources and concentration contributions in vehicles will be presented in the companion paper (Part II) based on the key information provided in this paper (Part I).

3.5. Limitations

In this study, chemical compounds from 6 to 12 carbons were sampled with Tenax TA tubes and analyzed using TD-GC/MS method. However, the VOCs that are out of the above-mentioned carbon ranges may also have significant influences on health and odor, such as semi-volatile organic compounds, hydroxyl compounds, and amine compounds. Although these compounds were not measured in this paper, they should be undoubtedly investigated in the subsequent research and added to the VOC list to make it more robust in practical applications.

4. Conclusions

This study aims to perform the important first step of VOC source apportionment, that is to determine which VOC species need to be concerned and their concentration levels in vehicle cabins. To that end, field investigations in new private-use vehicles were performed, and the following conclusions may be drawn from this study:

(1) Aliphatic compounds, carbonyl compounds, and aromatic compounds played a dominating role in the commonly observed VOCs in new private-use vehicles, constituted over 70.0% in numbers.
(2) A total of 41 compounds from 6 to 12 carbons were selected as the noteworthy VOC species in new vehicle cabins based on a consideration of prevalence, possible health risks, possible odors, characteristic nature, and high concentrations
(3) The obtained results were compared with those in the used vehicles. There was an apparent difference in detected VOC species between the new vehicles and the used ones, indicating they may have different emission sources.
(4) The concentration levels of benzene, toluene, and xylene were observed obviously lower than those in new vehicles manufactured approximately 15 years ago, indicating the improvement of air quality in new vehicles as time went by.
(5) Statistical analysis showed approximately half paired correlations were statistically significant among all the 820 [(41 × 40)/2] correlations, indicating these compounds may come from the same source or at least their composition was similar in the measured vehicles.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.buildenv.2020.106796.

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