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Variations in amounts and potential sources of volatile organic chemicals in new cars

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Abstract

This study examines inter-brand, intra-brand and intra-model variations in volatile organic chemical (VOC) levels inside new cars. The effect of temperature on interior VOC levels was examined using model automobiles with and without the air-conditioning running. Potential sources of VOC were assessed by comparing VOC levels with two interior trims (leather and fabric) and by analyzing VOC emissions from various interior components. Five brands of new car, both domestic and imported, were tested. Twelve targeted VOCs were collected on solid sorbents and analyzed using thermal desorption and GC/FID. VOCs from interior parts and adhesives were identified using solid phase micro-extraction (SPME) coupled with GC/MS. The VOC concentrations varied markedly among brands and within models, and individual VOC levels ranged from below the detection limit (a few μg per cubic meter) to thousands of μg per cubic meter. The intra-model variability (mean, 47%) in the VOC levels was approximately 50% that within each brand (mean, 95%). Although interior trim levels affected VOC levels, the effects differed among brands. Reduction of the cabin temperature reduced most VOC levels, but the impact was not statistically significant. Screening tests for VOCs from interior parts revealed that butylated hydroxytoluene (BHT), a common anti-oxidant, was the most common chemical. Long-chain aliphatic hydrocarbons, particularly C14–C17, were identified in most grease (lubricant) samples, and toluene and xylenes were ubiquitously present in adhesive samples. Process-related compounds, such as plasticizer, were also identified in interior parts. In-cabin VOC levels varied significantly among makes/models and interior trims. Concerned consumers should purchase older new cars from manufacturers since VOC levels inside car cabins normally declines over time. Improved processes or materials with lower VOC emission potential should be used to minimize in-cabin VOC sources for new cars.

Keywords: VOC; New car; Automobile; Cabin; Interior

1. Introduction

Automobile cabins are a relatively confined environment in which drivers/passengers are exposed to volatile organic chemicals (VOC), either off-gassing from interior components (Fedoruk and Kerger, 2003; Grabbs et al., 2000) or intruding from the surrounding environment (Chan et al., 1991a; Dor et al., 1995; Jo and Park, 1999; Lawryk et al., 1995). Such exposure is particularly significant in new cars, which have relatively high in-cabin VOC levels (Grabbs et al., 2000; Fedoruk and Kerger, 2003; Yoshida and Matsunaga, 2006). Concerns regarding contaminants inside car cabins also derive from the fact that people spend appreciable amounts of time inside automobiles. For example, US commuters spend an average of about

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90 min daily in automobiles (USEPA, 1997). Studies conducted in various regions have assessed the VOC exposures for commuters (Chan et al., 1991b, 2002; Dor et al., 1995; Duffy and Nelson, 1997; Jo and Park, 1999; Jo and Choi, 1996; Kingham et al., 1998; Leung and Harrison, 1999; Löfgren et al., 1991; Weisel et al., 1992), commercial drivers (Jo and Yu, 2001) and policemen (Riediker et al., 2003).

External VOC sources include emission/evaporation of un-combusted fuel or penetration of roadway air. In-cabin VOC levels are related to traffic density and inversely related to driving and wind speed (Weisel et al., 1992). Ventilation reduces interior VOC levels, but may alter the patterns of individual VOC between static and driving conditions (Fedoruk and Kerger, 2003). However, VOC associated with interior sources include those from upholstery (such as plastic moldings, carpet, seating surfaces, foam cushions, paint and sealants), detailing (such as cleaning substances, deodorizers, refreshers and surface treatment) and other sources (such as lubricants, smoking and microbes) (Fedoruk and Kerger, 2003; Grabbs et al., 2000; Jo and Yu, 2001; Rose et al., 2000; Yoshida and Matsunaga, 2006).

Apart from the potential long-term health effects, VOCs in new car cabins create a "new car odor", which is a nuisance to some occupants, and at high concentrations may evoke trigeminal responses of nasal pungency and eye irritation (Cometto-Muniz and Cain, 1990, 1994; Cometto-Muniz et al., 1997; Mølhave et al., 1991). Few studies have investigated the characteristics of VOC in new car cabins. One such study found over 60 VOC species in a new car cabin, with total VOC concentrations generally exceeding those in ambient air and also being highly variable. Moreover, the VOC species vary markedly among vehicles (Grabbs et al., 2000). The same investigation also found that the time of sampling substantially influenced VOC levels inside new cars since total VOC levels decreased by more than 90% during a 3-week test period. Another work to identify VOC species and their concentration–time characteristics identified 162 VOC and semi-VOC species in a new car. The sum of concentrations of all VOC on the day following delivery was approximately 14 mg/m^3, which greatly exceeding the proposed indoor VOC guideline of 300μg/m^3 (Seifert, 1995). The concentrations of most compounds declined over time, but increased with increasing interior temperature. A year later, the total VOC concentration was around one-tenth of its initial level (Yoshida and Matsunaga, 2006). These works have provided a basic understanding of VOC inside automobiles, but have limited applicability because of their small sample sizes.

This investigation addresses the following concerns regarding VOC concentrations in new cars. First, inter-brand and intra-brand variations in VOC levels were studied by making concurrent measurements in new cars from various manufacturers. Intra-model variations were examined using several cars of a particular make/model/trim and sharing the same date of manufacture. Additionally, the effect of temperature on interior VOC levels was investigated by testing the same automobile with and without air-conditioning. Finally, potential sources of VOC were evaluated by comparing the VOC levels between two interior trims (leather and fabric) and analyzing potential VOC off-gassing from various interior components, greases and adhesives.

2. Methods

2.1. Automobiles under evaluation

The vehicles studied comprised three domestic (Brands DO1, DO2 and DO3) and two imported brands (Brands IM1 and IM2). Domestic automobiles, which in this study were international brands that were domestically assembled, were manufactured within a few weeks to 3months before the study, while imports (both from E.U.) were manufactured over 4months before the study owing to delivery times. The models tested included sedan (SD), wagon (WN), sports utility vehicle (SUV) and coupe (CU). The size classes – full size (FS), mid-size (MS) and compact (CP) – were based on manufacturers' classifications. None of the tested vehicles underwent interior detailing or other treatment prior to sampling. All tests were conducted at local distribution depots in central Taiwan between March and November2004.

2.2. Test protocol

2.2.1. Sampling and analysis

The doors/windows of the tested vehicles were closed for at least 1 h before sampling (Grabbs et al., 2000). The air exchange rates of stationary vehicles (window closed, ventilation-off condition) were found to be 1–3 h^{-1} (Park et al., 1998). Accordingly, the influence from outside air on VOC levels was minimal. The sampling devices were set up on a laboratory ring-stand before sampling. During loading of sampling devices into each tested vehicle, the car doors were not opened for more than 10 s to reduce the interference from ambient air (Grabbs et al., 2000). Samples were taken close to the shoulder position of the driver's seat to ensure that

they reflected the conditions in the breathing zone of the driver. The method of analysis of VOC was modified from NIOSH (1996). Volatile organics inside car cabins were collected through multi-bed sorbent tubes (Model Carbotrap 300, Supelco/Sigma-Aldrich Inc., US) that were connected to portable sampling pumps (Model LFS-113DC, Gilian/Sensidyne Inc., US), and were analyzed using thermal desorption (Model ATD400, Perkin Elmer Inc., US) coupled with GC/FID (Model 6890plus GC, Hewlett Packard Inc., US). The multi-sorbent layout was employed to collect a wide range of volatile organics that are present in the environment. The sampling time was approximately 45 min and the sampling rate was ~150 ml/min. The sampling flow rate was ascertained by calibrating the flow rates of sampling pumps, using an air flow calibrator (Model DryCal DC-Lite, Bios International Corp., US), before and after the collection of each sample; a deviation of <5% was considered to be an acceptable criterion. The analysis selected 12 most commonly found organic chemicals as target compounds, which were selected according to the results of preliminary screening tests and the findings of the relevant studies (Grabbs et al., 2000; Fedoruk and Kerger, 2003). A capillary analytical column (Model HP-5 MS, 0.25 mm ID × 30 m, 1 μm thickness, Hewlett Packard Inc. US) was used for separation, with nitrogen as the carrier gas, running at 1.0 ml/min. The instrument's settings were as follows: the samples were desorbed at 330 °C for 10 min and the transfer line between the thermal desorption unit and GC was also set to 250°C, with the aid of an additional heater. The GC oven temperature program was as follows: initial temperature of 35°C/min, held for 10 min, rising to 220 °C, held for another 8 min. The mean desorption efficiency of the protocols exceeded 95% (based on spiked samples), while the mean relative standard deviation from laboratory duplicate measurements was under 18% across all target compounds. The method detection limits (MDLs), which is defined as the minimum amount of a substance that can be measured and reported within a 99% confidence that the analyte concentration is greater than zero (EPA, 1984), of toluene, ethylbenzene, *m&p*-xylene, *o*-xylene, styrene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene, *n*-undecane, tetradecane, butylated hydroxytoluene (BHT) and decane were 12.1, 32.8, 20.9, 17.2, 31.8, 9.2, 102, 64.4, 143, 271, 21.8, 33.6ng per sample, respectively, corresponding to air concentrations of 2.0, 5.5, 3.5, 2.9, 5.3, 1.5, 16.9, 10.7, 23.8, 45.2, 3.6, 5.6 μg/m^3, respectively, for a typical sample volume of 6.5 l. Ambient samples were also taken concurrently with each test to assess the background levels, which were subtracted from the samples. The test temperature and humidity were also recorded.

2.2.2. Tests of inter-brand, intra-brand and intra-model variation

Two domestic and two imported brands ($n=5$ for each) of vehicles were selected randomly and measured concurrently to estimate VOC level variations within and among brands. The four distribution depots from which samples were taken were located within a ~10 km radius. Multiple measurements ($n=3$) were made on two domestic models, with each test model taken from the same shipment (manufacturing date), to evaluate intra-model variations. Samples were collected under stationary conditions, with the engine off and windows closed.

2.2.3. Testing the effect of air conditioning (temperature)

The effect of temperature on in-cabin VOC level was tested by repeatedly making measurements of two domestic models, assuming negligible decay in VOC levels during sampling. The first samples were taken, with engines idling and windows closed, for about 45 min. The air-conditioning was then switched on, in re-circulated mode, for 5 min (for interior temperature to stabilize) before the second samples were taken (~45 min.). Besides individual VOC level, the total volatile organic compounds (TVOC) level was measured using a portable photo ionization detector (PID, Model PhoCheck 5000Ex, Ion Science Ltd. UK), which was calibrated using 100 ppm of iso-butene. The PID instrument was placed inside the cabin, adjacent to the ring-stand that holds the sampling device, and the data were recorded at 5-min intervals.

2.2.4. Testing the effect of trim

The effect of trim on interior VOC levels in two domestic models was tested. Six cars of each model were tested — three with leather and three with fabric trims; all six cars were from the same shipment (manufacturing date). The experiments were conducted under stationary conditions.

2.2.5. Evaluation of potential VOC sources

Interior parts, including door panels, carpets, roof lining, head-rests, rear deck panels and grease (for lubricating the seat mechanism) for three domestic models (mid-size SUV from DO1, compact sedan from DO2 and compact sedan from DO3) were purchased from local dealers to explore potential VOC sources. All parts were those of the latest models but the

manufacturing dates were unknown. Three adhesive samples obtained from an interior part manufacturer (Section 2.3) were also analyzed. A small piece (1 cm × 5 cm) of each test material was obtained, and loaded into a 22-ml head-space sample vial (except for the adhesive, of which 0.5-ml samples were loaded). After the test materials had been purged using a gentle flow of ultra high-purity nitrogen gas for 2 min, the vials were sealed. They were then equilibrated in a water bath at 40 °C for 30 min before analysis. Sampling was performed using the solid phase micro-extraction (SPME) technique coupled with GC/MS (Model 6890plus GC and 5973 MSD, Hewlett Packard Inc.) for analysis (Hippelein, 2006, 2004); specifically, a polydimethylsiloxane (PDMS) fiber with 100 μm-thick film (Supelco/Sigma-Aldrich Inc., US) was used to absorb (30 min) VOC from samples. The fiber was then desorbed at the injector of GC (250°C) for 5 min. The GC oven temperature program was as described above. Furthermore, the instrumental settings for the MSD (mass selective detector) were modified from NIOSH (1996). Specifically, electron impaction was used as the mass ion source, and was operated at 70 eV and 180 °C. The temperature of the transfer line between the GC and MS was also set to 250 °C. The collected chemicals were identified based on the similarity between the mass spectra index and that of the NIST/Wiley Library System, with a matching scale from 0 to 100. Only compounds with a matching quality of over 80 were reported.

2.3. Field visit to interior parts manufacturer

Field visits were made to an interior parts manufacturer (located in central Taiwan), which is a major supplier for domestic automobile manufacturers and produces primarily door panels and seats. The purpose of the visit was to understand the process/chemical involved in manufacturing interior parts and how manufacturing processes influence the subsequent VOC emission characteristics. Three adhesives (used to attach different portions of the door-panel moldings) were obtained to evaluate the VOC.

2.4. Statistical analysis

Concentrations of 12 targeted VOCs (round to two significant figures) and summary statistics (expressed as mean ± SD) were given for each test condition. Differences among VOC levels in various automobile brands and among cars of the same model were analyzed using ANOVA (analysis of variance) and Student's *t* tests, respectively. The effect of temperature on in-cabin VOC level was evaluated statistically using a paired *t* test. A value of $p<0.05$ was regarded as statistically significant.

3. Results and discussion

3.1. VOC concentrations inside new cars

This investigation evaluated the levels of 12 VOCs — aromatic (toluene, ethylbenzene, *m&p*-xylene, *o*-xylene, 1,3,5-trimethylbenzene, 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene, styrene), aliphatic (*n*-undecane, tetradecane, decane) and other (BHT). The concentrations varied markedly among brands and vehicles, and individual VOC levels ranged from below the method detection limits (a few $\mu g/m^3$) to thousands of $\mu g/m^3$ (Tables 1–3). These levels were within the ranges found in previous studies of VOC levels in new cars (Grabbs et al., 2000; Yoshida and Matsunaga, 2006), but were one to three orders of magnitude higher than those for commuters in older cars (Chan et al., 1991b, 2002; Dor et al., 1995; Duffy and Nelson, 1997; Jo and Park, 1999; Jo and Choi, 1996; Kingham et al., 1998; Lawryk et al., 1995; Leung and Harrison, 1999; Löfgren et al., 1991; Weisel et al., 1992). The analytical results (Table 1) also revealed that the toluene level was highest in Brands IM2 and DO1, while total xylene level was highest in Brands IM1 and DO2.

3.2. Inter- and intra-brand variations in VOC concentrations

Concurrent measurements were made in various vehicles, regardless of manufacture dates, of four brands to obtain general information about levels and variations of VOC concentrations in new cars. The measurement results (Table 1) indicated statistical differences ($p<0.05$, ANOVA test) in VOC levels among brands, specifically for toluene, xylenes, 1,2,4- and 1,2,3-trimethylbenzene and tetradecane. Such differences did not exist between the two domestic brands, except for 1,2,4-trimethylbenzene, but were apparent between domestic and imported cars. Imported automobiles generally had lower average VOC levels than domestic automobiles, but only three compounds, namely, toluene, *m&p*-xylenes and 1,2,3-trimethylbenzene, reached statistically significant levels ($p<0.05$, *t* test). Significant variations were observed within brands.

For example, for brand DO2, the concentration of toluene ranged from 280 to 5500 $\mu g/m^3$ and that of *m&p*-xylenes ranged from ND (below the detection limit) to 7900 $\mu g/m^3$. The mean coefficients of

Table 1
VOC concentrations (μg/m³) in various new domestic and imported automobiles

Compounds	IM1[a]						IM2				DO1				DO2							
	SD[b]	WN	SD	CU	SD	Mean± SD	SD	SUV	SUV	SD	SD	Mean± SD	SD	SD	SD	SD	Mean± SD	WN	WN	WN	SD	Mean± SD
	FS, L	CP, SL	MS, SL	CP, SL	FS, L		MS, L	CP,L	MS,L	CP, L	FS, L		MS, L	MS, L	CP, L	CP, L		MS, L	MS, L	MS, F	CP, F	CP, L	
Toluene*	70	32	49	ND[c]	17	34±27	96	230	260	320	150	210±91	1010	240	2200	5700	4600	2700±2300	550	3100	280	530	450	2000±2300
Ethylbenzene	ND	130	ND	10	190	66±87	22	35	36	82	36	42±23	47	ND	240	230	170	140±110	170	ND	ND	ND	ND	35±74
m&p-Xylene*	260	270	190	ND	ND	140±140	25	24	59	170	150	78±62	85	15	340	460	230	230±180	2400	7900	1500	2100	ND	2500±1400
o-Xylene*	47	160	58	ND	ND	53±65	13	13	30	84	58	39±31	43	8.1	170	380	110	140±150	1200	4000	740	1100	ND	1400±1500
Styrene	260	140	220	12	14	130±110	110	44	16	55	46	54±35	240	39	320	400	110	140±380	4900	2700	ND	59	16	1500±2200
1,3,5-Trimethylbenzene*	50	86	68	12	11	45±34	19	33	ND	68	63	37±29	120	21	ND	ND	ND	28±52	260	74	14	ND	23	75±110
1,2,4-Trimethylbenzene*	27	180	54	48	58	73±59	14	ND	13	ND	110	30±45	420	22	860	710	480	500±320	75	75	16	ND	33	41±33
1,2,3-Trimethylbenzene*	23	28	40	52	23	33±13	36	401	ND	38	130	50±45	34	8.4	480	510	480	300±260	360	290	75	49	92	170±140
Decane	98	170	110	24	33	87±61	32	58	58	120	ND	54±42	330	30	ND	ND	ND	75±150	68	27	17	26	13	30±22
n-Undecane	110	120	200	10	11	90±81	7.5	28	63	52	28	36±22	17	43	47	48	50	41±14	210	190	56	46	120	130±76
Tetradecane*	35	75	35	ND	ND	29±30	ND	ND	9.4	ND	ND	2.8±3.7	23	28	290	300	34	140±150	ND	ND	ND	ND	ND	NA
BHT	ND	ND	ND	ND	ND	NA	ND	ND	ND	ND	ND	NA	ND	ND	62	27	74	33±33	ND	ND	ND	ND	ND	NA

[a] IM = import; Do = domestic; test condition: 32.0 °C, 56% RH.
[b] SD = sedan; WN = wagon; SUV = sports utility vehicle; CU = coupe. FS = full size; CP = compact; MS = mid-size; L = leather trim; SL = synthetic leather trim; F = fabric trim.
[c] ND = not detectable; NA = not available.
* Statistically significant (ANOVA test, $p<0.05$).

variation (CV) for the compounds tested were 88, 83, 100 and 110% for brands IM1, IM2, DO1 and DO2, respectively (mean, 95%). The within-brand variations were smaller for imports, which also had lower overall VOC levels. In-cabin VOC levels of new cars are a function of the time lapsed following manufacture, temperature (Yoshida and Matsunaga, 2005), rate of exchange of interior air with surrounding environment (Park et al., 1998) and interior layout (Grabbs et al., 2000), including VOC emission characteristics and habitable volume. This study controls for the potential effect of temperature by taking of measurements in the surrounding area on the same day, and testing for the significance of the effect of brand (time). The results demonstrate that the inter-brand variation in VOC levels (particularly for aromatics) is statistically greater than intra-brand variation, which is attributable to other un-controlled factors, including air exchange and interior layouts.

The results were consistent with previous findings that VOC levels inside new car cabins decrease rapidly following delivery and that large variations exist among brands (Grabbs et al., 2000). Domestic vehicles were newer (being tested a few weeks to a few months after their manufacturing date) than imports, which were tested at least 4 months after their manufacture due to shipping time, and thus exhibited higher overall VOC levels.

3.3. Intra-model variation in VOC concentrations

Intra-model variations in VOC level were estimated using four specific domestic models ($n = 3$ for each); the tested vehicles of each model were manufactured on the same date. The results (Table 2) showed that the intra-model variation in VOC levels varied across model; for example, the coefficient of variation of VOC levels in Sedan1 ranged from 11% for ethylbenzene to 150% for *n*-undecane. The mean CVs for the evaluated compounds were 41, 48, 45 and 56% for the four test models, SUV with leather trim (Brand DO1), SUV with fabric trim (Brand DO1), sedan with leather trim (Brand DO2) and sedan with fabric trim (Brand DO2), respectively. These results indicated that intra-model variability (mean, 47%) in VOC levels was about 50% of the intra-brand variability (mean, 95%).

3.4. Effect of interior trim levels on VOC concentrations

The impact of interior trim on VOC levels was evaluated by testing the same models with leather or fabric trims. Three cars of each model with the same

Table 2
VOC concentrations (μg/m^3) in the same automobile models with different trim levels

Compounds	SUV (DO1, MS) [a]							Sedan (DO2, CP)						
	Leather trim				Fabric trim			Leather trim				Fabric trim		
	1	2	3	Mean±SD	1	2	3	Mean±SD	1	2	3	Mean±SD	1	2	3	Mean±SD
Toluene	7500	3000	8300	6300±200	1100	940	3900	2000±1600	290	260	350	300±44**	2600	1800	1800	2100±470**
Ethylbenzene	69	52	110	77±29	ND	27	75	34±37	110	130	140	130±15	2300	900	1600	1600±700
m&p-Xylene	200	220	56	160±88	36	28	140	68±63	ND	ND	ND	NA	11000	7600	8700	9000±1500**
o-Xylene	99	110	29	79±44	19	15	71	35±31	ND	ND	ND	NA	5200	3800	4300	4400±740**
Styrene	310	160	340	270±95	98	100	260	150±91	16	15	22	18±38**	6900	4100	5300	5400±1400**
1,3,5-Trimethylbenzene	39	75	43	52±20	32	28	78	46±28	9.5	21	290	110±160	250	29	290	190±140
1,2,4-Trimethylbenzene	740	360	632	580±200*	160	26	21	69±80*	13	44	17	25±17	2100	14	980	1000±1100
1,2,3-Trimethylbenzene	190	130	160	160±31	65	30	150	80±60	43	51	55	50±6.6	530	140	84	250±240
Decane	95	50	43	62±28	88	130	540	250±250	30	17	34	27±9.1	2	53	120	65±45
n-Undecane	38	15	26	26±11	140	13	230	130±110	70	73	86	76±8.2	120	65	400	200±180
Tetradecane	ND	ND	ND	NA	ND	70	110	60±55	6.3	ND	13	6.7±5.7	ND	ND	N	NA
BHT	ND	ND	ND	NA	74	ND	ND	25±42	21	17	36	25±9.8	ND	ND	ND	NA

*, **Statistically significant (*t* test, $p<0.05$).
[a] DO = Domestic; CP = compact; MS = mid-size; test condition = DO-01:30.9 °C, 43% RH; DO-02:30.7 °C, 53% RH.

date of manufacture were tested. The test results (Table 2) revealed that sedans with fabric trim (Brand DO2) generally had higher VOC levels than those with leather interior, with the levels of toluene, xylenes (total) and styrene reaching statistically significant level ($p<0.05$). For the other model (SUV, DO1), VOC levels in vehicles with leather trim were higher than those for their fabric counterparts, but only that of 1,2,4-trimethylbenzene was statistically significant ($p<0.05$). These findings clearly demonstrated that interior trim affected VOC levels inside the cabins, but the effect varied among brands.

These data also indicated that xylenes (total) were the most abundant VOC species in sedans with fabric trim, but were below the detection limit in the same models with leather trim (Brand DO2, Table 2). However, the toluene concentration in SUVs (Brand DO1, both trim levels), exceeded that of other VOC. A previous study of VOC levels in an approximately 2-week old automobile (similar to those used in this sub-test), found that concentrations of xylenes (total) were highest (with levels of toluene, ethylbenzene and xylenes (total) reaching 225.8, 360.9 and 4002.9 μg/m^3, respectively), on the first day following delivery (Yoshida and Matsunaga, 2006). Hence, different manufacturing processes, such as those using different organic solvents or components, from various brands substantially influence the dominant VOC species and their levels in new cars.

3.5. Effect of air conditioning (temperature) on VOC concentrations

Earlier work has demonstrated that increasing the temperature increased VOC levels inside car cabins (Fedoruk and Kerger, 2003). This investigation thus examined whether lowering temperature by means of air conditioning reduced in-cabin VOC levels. The analytical results (Table 3) indicated that reducing in-cabin temperature (on average, from 29 to 23°C) reduced most VOC levels inside the tested automobiles, but the reduction was not statistically significant ($p>0.05$, paired *t* test), except in a few cases, mainly for Brand DO1, in which VOC levels of some species increased after the air-conditioning system was used. Total VOC levels, measured using a direct-reading PID instrument, also declined in six out of eight cars but were not statistically significantly ($p>0.05$, paired *t* test).

Air infiltration, either from air-conditioning system or exhaust emission probably confounded these measurements since the tests were conducted under stationary and idling conditions. The levels of gasoline-

Table 3
VOC concentration (μg/m^3) in various new vehicles, with and without the air-conditioning on

Compounds	DO2								DO1					
	WN (MS)-L		WN (MS)-L		WN (MS)-L		SD (CP)-L		SUV(MS)-L		SUV(MS)-L		SUV(MS)-L	
	Air/off	Air/on	Air/off	Air/on	Air/off	Air/on	Air/off	Air/on	Air/off	Air/on	Air/off	Air/on	Air/off	Air/on
	30.7 °C	26.6 °C	30.6 °C	27.1 °C	32.2 °C	27.8 °C	31.8 °C	26.6 °C	25.1 °C	20.1 °C	25.6 °C	20.4 °C	26.4 °C	19.6 °C	26.6 °C	18.6 °C
Toluene	10000	2300	820	720	730	700	510	290	3900	3700	2400	2300	460	590	530	710
Ethylbenzene	3700	580	300	190	430	310	90	12	26	130	53	89	ND	ND	14	ND
m&p-Xylene	4400	300	2900	560	3800	2200	850	ND	37	260	130	240	ND	15	43	19
o-Xylene	1800	1500	1400	270	1900	1100	420	ND	9.1	120	52	110	ND	15	43	20
Styrene	2300	1000	1000	420	1600	710	320	29	280	320	120	170	36	31	39	35
1,3,5-Trimethylbenzene	870	100	34	ND	44	ND	14	ND	56	130	76	120	19	27	ND	26
1,2,4-Trimethylbenzene	500	160	ND	53	ND	62	ND	57	53	170	150	210	53	59	53	60
1,2,3-Trimethylbenzene	730	120	61	50	50	30	23	25	62	37	120	170	39	27	ND	26
Decane	ND	ND	130	ND	170	ND	79	33	320	710	520	620	130	150	97	140
n-Undecane	230	190	160	32	39	130	240	150	160	230	260	250	110	100	100	110
Tetradecane	34	27	27	16	160	54	260	54	260	130	ND	ND	ND	ND	ND	ND
BHT	27	19	25	86	100	ND	43	ND	ND	ND	ND	ND	ND	ND	ND	ND
Total VOC (ppm)[a]	28±0.4	3.1±0.1	5.2±0.0	2.5±0.1	6.6±0.1	4.5±0.2	4.7±0.1	4.1±0.1	5.4±0.0	6.8±0.0	5.4±0.0	6.6±0.1	2.5±0.0	1.7±0.1	2.7±0.2	1.5±0.0

[a] Total volatile organic compounds (ppm) were measured and recorded every 5 min, and overall mean±SD was presented.

related chemicals, particularly decane, increased significantly in all four Brand DO1 test vehicles, suggesting possible contamination from nearby automobile exhaust and built-up inside the cabins. This finding is further verified by the fact that the parking depot, where Brand DO1 cars were tested, was roofed and not as well vented as that the parking depot of the Brand DO2 counterparts.

These findings suggest that the use of air conditioning generally reduced the in-cabin VOC levels by reducing the interior temperature or dilution, but interference from air intrusion is also possible. Accordingly, the effect of air conditioning on interior VOC warrants further investigation.

3.6. Potential VOC sources

Interior components, such as plastic moldings, upholstery, carpeting, adhesives, lubricants and other, are presumably the main sources of VOC inside new car cabins. For example, a polymer solvent (1-methyl-2-pyrrolidone) and a catalyst in the production of PU (1,4-diazabicyclo[2,2,2]octane), which are hardly detectable in the residence air, have been detected in new cars. They are considered to be characteristic compounds in car interiors where plastics, rubbers and resins are abundant (Yoshida and Matsunaga, 2006; Fedoruk and Kerger, 2003). Therefore, this study surveyed interior parts for VOC. Notably, since the manufacture dates of the test materials were unknown (even though these parts were from the latest model), this screening test was not intended to examine the emission/decay rate of VOC from these materials, nor to ascertain the sources of 12 target VOCs, as the parts were not taken directly from the tested vehicles. Rather, this work employed headspace and SPME protocols, which have greater analytical sensitivity than the standard static headspace approach, to elucidate the VOC species from particular materials of each interior part. Nonetheless the chemicals identified herein may not be exhaustive due to analytical limitations.

The analytical results (Table 4) revealed that 2,6-di-tert-butyl-4-methylphenol, otherwise known as butylated hydroxytoluene (BHT), a common anti-oxidant in petroleum products, synthetic rubbers and plastics, was the most common chemical (found in 16 out of 27 samples) in the interior parts tested, followed by aliphatic hydrocarbons, such as heptadecane, hexadecane and tetradecane.

Long-chain aliphatic hydrocarbons, particularly C14–C17 hydrocarbons (namely tetradecane, pentadecane, hexadecane and heptadecane, respectively), were identified in most grease (as lubricant) samples. This

Table 4
VOC identification in various interior parts from three domestic automobile models

Compounds	Interior components																										
	Grease			Trim (calf)			Trim (fabric)			Trim (synthetic leather)			Seat foam			Door panel[a]			Roof lining			Carpet			Rear panel		
	DO1[b]	DO2	DO3	DO1	DO2	DO3	DO1	DO2	DO3	DO1	DO2	DO3	DO1	DO2	DO3	DO1	DO2	DO3	DO1	DO2	DO3	DO1	DO2	DO3	DO1	DO2	DO3
Butylated hydroxytoluene[c]	+	+	+		+		+	+		+		+	+		+		+			+			+		+	+	+
Cyclohexanone					+					+							+										
Diisopropylnaphtalene																+											
Docosane																									+		+
Dotriacotane										+																	
Eicosane																							+		+		
1-Ethyldodeccyl-benzene					+																						
1-Ethyldodeccyl-benzene					+																						
Heptane			+																								
Heptadecane		+			+																	+	+		+		
Hexadecane		+			+																		+			+	+
0-Hydroxybiphenyl					+																						
2-Hydroxy-benzaldehyde																										+	
1-Methyl-2pyrrolidinone														+													
Naphthalene																										+	+
2-Methyl-naphthalene																										+	
2,3-Dimethyl-naphthalene																										+	
2,7-Dimethyl-naphthalene																										+	
1,4,6-Trimethyl-naphthalene																										+	
Nonadecane																							+				
Pentadecane		+																							+		+
4-Chloro-methyl phenol					+																						
Phenol																										+	
Teradecane	+	+	+		+														+							+	
Toluene																				+							
Tri(2-chlorothyl) phosphate					+																						
Triethylenediamine																			+								
4-Chloro-3-methyl-phenol					+																						

[a] Upper PVC film portion.

[b] Represents different manufacturers.

[c] Compounds with mass spectra match quality (based on the NIST/Wiley Library System) greater than 80 are listed.

finding verified previous speculation that heavier (long-chain) alkanes that are present in the car cabin are emitted from the greases that are used to lubricate mechanical parts such as seat rails (Grabbs et al., 2000). However, other long-chain aliphatics, such as eicosane (C20) and docosane (C22), which are usually applied as plasticizers or synthesis materials, were identified in carpet and rear panel samples.

A wide range of VOC was present in the three adhesive samples that had been obtained from a local interior part manufacturer (Table 5). Specifically, four to 38 chemical species were identified in the three adhesives tested, and toluene and xylenes (total) were present in all three samples. This result explains why toluene and xylenes are present in the car cabins at high concentration (Tables 1–3), but nearly completely undetected in the interior parts under evaluation (Table 4) since most of the tested materials did not contain adhesive layers. Similarly, trimethylbenzene(s) found in the car cabins (Tables 1–3) and naphthalene(s) detected in a rear panel sample (Table 4) may also originate from the adhesive. Thus, the adhesives that are used to manufacture various interior parts are probably the major sources of toluene, xylenes, and the other chemicals that are detected inside the cabins.

During the visit to the interior part factory, the moldings used in automobile cabin were found to consist of various materials, including poly-urethane (PU) foam, poly-propylene (PP) plastic, acrylonitrile butadiene styrene (ABS) resin, poly-vinyl chloride (PVC) plastic, leathers (natural and synthetic) and synthetic fibers. Some of these, such as PU and PP, are manufactured on-site from raw materials. Various adhesives are utilized to attach the various components of door panels because of different adhesion between materials. For instance, a polychlorobutadiene-type, general-purpose adhesive was employed to attach a leather sheet to a base plate and then to the middle part of the door-panel frame (mostly made of PP), while a PU/isocyanate-type adhesive was used to hold the upper portion of the door panel, which comprises a PVC surfacing and underlying foam, to the panel frame. Therefore various adhesives employed in the manufacturing processes will influence the VOC species and emission characteristics inside the cabins.

Moreover, chemicals that are associated with the manufacture of molding and upholstery materials were also identified in interior samples. For example, 1-methyl-2-pyrrolidinone (or 1-methyl-2-pyrrolidone), a plasticizer and polymer solvent that is used to manufacture seat poly-urethane (PU) foam, was identified in one of the seat foam samples. This chemical was also present in two previously tested new automobiles, and has been regarded as a characteristic compound in car interiors where plastics, rubbers and resins are widely used (Fedoruk and Kerger, 2003; Yoshida and Matsunaga, 2006). Triethylenediamine (TEDA or 1,4-diazabicyclo[2,2,2]octane), a common catalyst that is used in the manufacture of all PU foams, has been identified in a new car (Yoshida and Matsunaga, 2006) and in one roof lining sample, which is made of synthetic fiber and PU foam. Cyclohexanone, a multi-purpose solvent (for cellulose acetate, vinyl resins, crude rubber and waxes) and an intermediate in the production of nylon was detected in leather (both natural calf and synthetic) and door-panel samples (upper portion).

Table 5
VOC identified in various adhesives used to manufacture interior parts

Adhesive type	Usage [a]	VOCs identified [b]
Acrylic	A	Toluene; xylene (and isomers)
PU/isocyanate	B	Toluene; xylene (and isomers), ethyl acetate
Polychlorobutadiene	C	• Aromatic Toluene; ethylbenzene; xylene (and isomers); isopropyl-benzene; trimethylbenzene (and isomers); 1-methyl-3propyl-benzene; 1-ethyl-3,5-dimethyl-benzene; 2-ethyl-1,4-dimethyl-benzene (and isomers); 1-methyl-3-isopropyl-benzene (and isomers); 1,2,3,4-tetramethyl-benzene (and isomers); 2,4-diethyl-1methyl-benzene (and isomers) • Aliphatic 2,2-dimethyl-butane; 2-methyl-pentane; 3-methyl-hexane; *n*-heptane; *n*-octane; cyclotetradecane; 1-methyl-3ethyl-cyclopentane; ethyl cyclohexane • PAHs Naphthalene; 1,2-dihydro-naphthalene; 2-methyl-naphthalene • Others butylated hydroxyltoluene (BHT, and isomers); diethyl phthalate; isooctyl phthalate; hexadecanal

[a] Compounds with mass spectra match quality (based on the NIST/Wiley Library System) greater than 80 are listed.
[b] A: for ABS material; B: for PVC material; C: multi-purpose.

The identification of specific VOC species from individual interior parts provides evidence of their potential sources.

4. Implications of findings

The concentrations of the individual VOC species in new cars that were measured herein, ranging from a few to more than ten thousands μg/m^3, markedly exceeds the proposed indoor VOC guidelines, particularly for aromatic (50 μg/m^3) and alkanes (100 μg/m^3) (Seifert, 1995). Additionally, some of the VOCs that have been found in new car cabins such as BHT are eye and respiratory tract irritants (ACGIH, 2003). Accordingly, the exposure of occupants to these VOC must be reduced. Various factors are known to influence VOC levels inside new car cabins. For instance, the concentrations of most VOC declined over time, but increased with interior temperature. However, time had a stronger effect than interior temperature in reducing the concentrations of aromatic compounds, as the concentrations inside new cars decrease rapidly and significantly following delivery/manufacture (Yoshida and Matsunaga, 2006; Grabbs et al., 2000). Hence, purchasing older new cars from the manufacturer would be especially beneficial in minimizing exposure to aromatic VOC, as demonstrated in this investigation (Table 1). Meanwhile, seasonal variations in in-cabin VOC levels resulting from differences in ambient temperature are expected for particular VOC, such as aliphatic hydrocarbons, over several (4–5) years following delivery/manufacture (Yoshida and Matsunaga, 2006). The use of air-conditioning, which reduces interior temperature, generally reduces in-cabin VOC levels. Nonetheless this reduction may be confounded by other factors, such as the exchange of the internal air with ambient air.

The manner of vehicle usage, for example, parking in sunlight, can increase the interior temperature and promote the emission of VOC. A high temperature may also induce photo-chemical reactions and subsequently generate new VOC species, which contribute to in-cabin VOC levels. For example, phthalate chemicals (commonly used polymer accelerators/plasticizers) that have been identified in current door-panel and adhesive samples can be transformed to 2-ethyl-1-hexanol via hydrolysis and thermal degradation (Wolkoff, 1999; Sollinger et al., 1994). 2-Ethyl-1-hexanol is believed not to originate from interior components since the in-cabin concentration increased considerably following delivery (Yoshida and Matsunaga, 2006), and after the interior temperature increased from ~100 to 145 °F (Fedoruk and Kerger, 2003).

Interior trim also contributes to in-cabin VOC since various materials and adhesives used in manufacturing interior moldings and upholstery have different VOC emission characteristics. Hence different automobiles from various brands with different trims are expected to have different in-cabin VOC species and levels, as evident in this investigation. Nevertheless, relatively large variations (mean CV, 47%) in VOC levels were also noted in vehicles that are of the same make/model/trim and have the same manufacturing date. Minor variations in the manufacturing process/parts or use of interior parts with different manufacturing dates are possible causes of such intra-model variations.

The exchange of air between ambient and car interior also affects in-cabin VOC. Measurements of VOC in new cars (including this study) were generally under stationary conditions, under which the air exchange rate was relatively low (1–3 h^{-1}) (Park et al., 1998). However, other operating conditions such as setting the fan to fresh air (with windows closed) increase the air exchange rate (13.3–26.1 h^{-1}) and thereby reduce the in-cabin VOC levels. Similarly, driving, regardless of the ventilation mode, caused a 4- to 20-fold reduction in VOC levels after a 90-min trip, suggesting significant air turn-over (Fedoruk and Kerger, 2003; Ott et al., 1992). However, driving also altered in-cabin VOC patterns, from those dominated by C9 alkyl benzenes (emitted from the interior) to those dominated by C6–C9 alkane (un-burned VOC from exhaust), revealing an exchange of air with the outside (Fedoruk and Kerger, 2003). Accordingly, increasing cabin ventilation reduced VOC levels in the interior, but at the cost of introducing other air contaminants from outside the cabin.

5. Conclusions

Previous studies have demonstrated that VOC levels inside new car cabins markedly exceed those in older cars, and that large variations in concentrations existed among new cars. This work assessed the between-brand, within-brand and intra-model variabilities of in-cabin VOC. Emissions from interior components are the main sources of in-cabin VOC for new cars. Therefore unsurprisingly, VOC characteristics differed among new automobiles of various makes/models with different interior trims. Intra-model variability in VOC levels (mean, 47%) was approximately 50% less than intra-brand variability (mean, 95%). Older new cars (imported cars herein) have significantly lower VOC concentrations – especially for aromatic compounds, such as toluene and xylenes – than domestic automobiles

since the levels of these compounds were found to decay rapidly following manufacture/delivery.

Screening tests for VOC from interior parts demonstrated that the grease used to lubricate mechanical parts is the most likely source of long-chain (C14–C17) alkanes inside the car cabin, while the adhesives used to attach interior moldings are the main sources of in-cabin toluene and xylenes. Identifying process-related compounds, such as plasticizers and catalysts from interior parts, and various aromatic and aliphatic VOC from adhesives, suggests that improved processes or materials with lower VOC emission potential should be effective in minimizing VOC. However, until such processes/materials become available, exposure should be reduced since in-cabin VOC levels clearly exceed the proposed indoor VOC guidelines. Practically, concerned consumers can purchase older new cars from the manufacturer since VOC intensity inside car cabins generally declines over time. The use of air conditioning, which reduces interior temperature and emission potential, may also reduce the levels of VOC inside new car cabins.

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