



Variation of VOCs inside a New Car during the First Year and Their Relationship to Temperature

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Abstract

Passenger exposure to volatile organic compounds (VOCs) emitted from vehicle interiors has increasingly drawn public concern over their potential health risks. This study aimed to investigate ambient levels of in-cabin VOCs in a new car over the period of one year after first delivery. The relationship between VOC concentrations and in-cabin temperature was also studied. Seventeen active air samplings inside a parked new car were conducted from February 2012 to February 2013 using sorbent tubes. Six VOCs were measured with first-month average concentrations of $215 \mu\text{g}/\text{m}^3$ for benzene, $65.6 \mu\text{g}/\text{m}^3$ for toluene, $151 \mu\text{g}/\text{m}^3$ for 1,2,3-trimethylbenzene, $806 \mu\text{g}/\text{m}^3$ for ethyl acetate, $183 \mu\text{g}/\text{m}^3$ for formaldehyde, and $28.2 \mu\text{g}/\text{m}^3$ for acetone. The concentration profiles of all VOCs except formaldehyde declined, falling below the detection limits towards the end of the 1-year monitoring period. Formaldehyde concentrations were found to be directly proportional to in-cabin temperature at a significance level of $p=0.05$ during the first five months.

Keywords: VOCs; car interiors; vehicle indoor air quality

Introduction

People in middle-class societies are reported as spending an average 87% of their time indoors and 7% in transit [1]. Due to increasingly severe traffic problems in most urban cities, time spent in vehicle is increasing. In Bangkok, Thailand, average driving speeds of passenger cars on main roads in July 2012 were 17.9 and 21.6 km per hour during morning and evening rush hours, respectively [2], with average commuting times of two

hours from home to work and back in Bangkok [3]. The significance of passenger exposure to airborne pollutants in vehicle cabins has increased not only because of these longer commuting times, but also because of the worsening levels of vehicle indoor air quality (VIAQ). The cabin of an automobile contains a variety of materials such as trims, rubber, carpets, floor mats, polyurethane foam, adhesives, paints, varnishes, solvents, plastics and synthetic fibers [4]. Such materials can

emit a variety of VOCs such as aliphatic hydrocarbons, aromatic hydrocarbons, carbonyls, esters and terpenes, some of which are toxic to humans whilst others and some such as benzene are linked to cancer [5]. Therefore, vehicle manufactures in some countries have set up voluntary programs targeting VIAQ; these include the programs of the Japanese Automotive Manufacturers Association (JAMA) and the German Automotive Industry Association (Verband der Automobil industrie, VDA). Emission characteristics of VOCs from vehicle interiors depend on several factors including type of material used, car age or mileage, in-cabin temperature, and gas-phase or interface chemistry. In Thailand, no studies have been conducted to investigate VOCs in the cabins of new, domestically manufactured automobiles. The objectives of this study were therefore to measure levels of in-cabin VOCs of a new car and determine VOC concentrations in relation to in-cabin temperatures.

Materials and methods

The test vehicle was a new Japanese subcompact car purchased by the Faculty of Engineering, Mahasarakham University, Thailand for use by the Faculty. It was delivered to the Faculty directly ex-factory on 8 February, 2012. In-cabin air sampling began 7 days post-delivery. 17 air samples were collected in the afternoons over a 368-day period from 15 February 2012 to 24 February 2013. During the study period, the car was regularly used except on the sampling dates. No smoking was allowed in the car. No articles other than the interior materials of factory origin were brought into the cabin. However, the original rubber carpets were replaced with larger ones purchased from the market before the sampling date of the 108th day. A solid air freshener was also brought into the cabin and a new CD player was installed about two

weeks before the sampling date of the 170th day. However, the air freshener was removed and the in-cabin air vented for three hours prior to air sampling. When not in use, the car was normally parked in front of the Faculty building without a shading roof.

To begin the sampling course, the test car was moved and parked in a sunny outdoor location away from traffic and outdoor sources of pollutants. All windows were opened to vent the in-cabin air for ~0.5 hour, then closed for ~2-3 hours to allow the in-cabin VOCs to reach a steady state. The target airborne organic compounds were benzene, toluene, 1,2,3-trimethylbenzene, ethyl acetate, formaldehyde, and acetone. Glass tubes, 70 mm, 7-mm o.d., containing two sections of 100/50 mg of 20/40 mesh size charcoal (SKC Inc., USA), were used to collect the aromatics and ethyl acetate, while cartridges filled with 60/80 mesh dinitrophenylhydrazine (DNPH) coated silica gel (SKC Inc., USA), were used to collect formaldehyde and acetone. Personal sampling pumps (SKC Inc., USA) were used to draw gas samples to sorbent tubes at a flow rate of ~0.2 L/min for 3-4 hours during ~1 p.m. to ~5 p.m. Duplicate samples were collected to enhance sample reliability and analytical methods. The sampling point was ~60 cm above the car floor. The temperature inside and outside the test car was also measured at the sampling time with a Testo[®] 608-H1 (Testo Inc., Germany) and a Hanna[®] HI 9564 (Hanna Instruments, USA). Table 1 summarizes the 17 in-cabin air samplings. Note that the last two samplings on 3 and 24 February 2013 were performed with only charcoal samples.

VOCs adsorbed on the charcoal were extracted with 1 mL of carbon disulfide (Merck & Co., USA) and analyzed by gas chromatography/mass spectrometry (GC/MS). Carbonyls adsorbed on the DNPH cartridges

Table 1 Details of in-cabin air samplings

Sampling No.	Sampling date (d/m/y)	Car age (day)	Odometer (km)	In-cabin temperature (°C)	Outdoor temperature (°C)
1	15/2/12	12	371	33.3	32.4
2	22/2/12	19	376	35.0	30.7
3	3/3/12	29	1319	44.8	38.5
4	10/3/12	36	1933	33.6	34.4
5	24/3/12	50	3257	29.4	26.5
6	1/4/12	61	3264	30.3	30.9
7	17/4/12	74	3269	35.7	32.1
8	29/4/12	86	3280	40.2	35.3
9	21/5/12	108	5198	44.0	39.6
10	3/6/12	121	5420	43.3	39.3
11	1/7/12	149	5982	38.4	38.3
12	21/7/12	170	8921	44.8	44.1
13	28/9/12	249	14221	47.8	45.3
14	18/11/12	270	15094	38.8	39.3
15	6/12/12	298	16592	44.3	41.8
16	3/2/13	347	19036	36.9	35.2
17	24/2/13	368	20865	46.1	45.1

were extracted with 2 ml of acetonitrile (Merck & Co., USA) and analyzed by high performance liquid chromatography (HPLC). The conditions of GC/MS and HPLC were as described in previous studies [6, 7]. The sampling and analytical methods followed the NIOSH manual of analytical methods for aromatic hydrocarbons [8] and the US EPA compendium of methods for the determination of formaldehyde [9]. A five-point calibration was performed for the GC/MS analyses including 0, 10, 20, 50, and 100 $\mu\text{g/ml}$ with the R-squared value of 0.986-0.997. A four-point calibration was performed for the HPLC analyses including 0, 0.1, 0.5, and 1 $\mu\text{g/ml}$ with the R-squared value of 0.997-0.999. The method detection limits (MDL), which followed the US EPA [10] guideline procedure were 23, 5.9, 6.0, 5.8, 26, and 3.8 ng for benzene, toluene, 1,2,3-trimethylbenzene, ethyl acetate, formaldehyde, and acetone, respectively.

SPSS[®] version 15.0 for Windows was used to perform Pearson test for determining linear association between the in-cabin temperature and concentrations of the six VOCs measured during the sampling period of the first five months.

Results and discussion

1) VOC concentrations with respect to car age

Figure 1 shows in-cabin concentrations of the six VOCs during the monitoring period of 368 days, except for formaldehyde and acetone, for which the monitoring period was 298 days. Since no articles were brought into the car cabin, the major sources of VOCs detected were assumed to be from the interior materials used in manufacture. Aromatics were found to be present at a level of 70-300 $\mu\text{g/m}^3$ in the first month following delivery ex-factory.

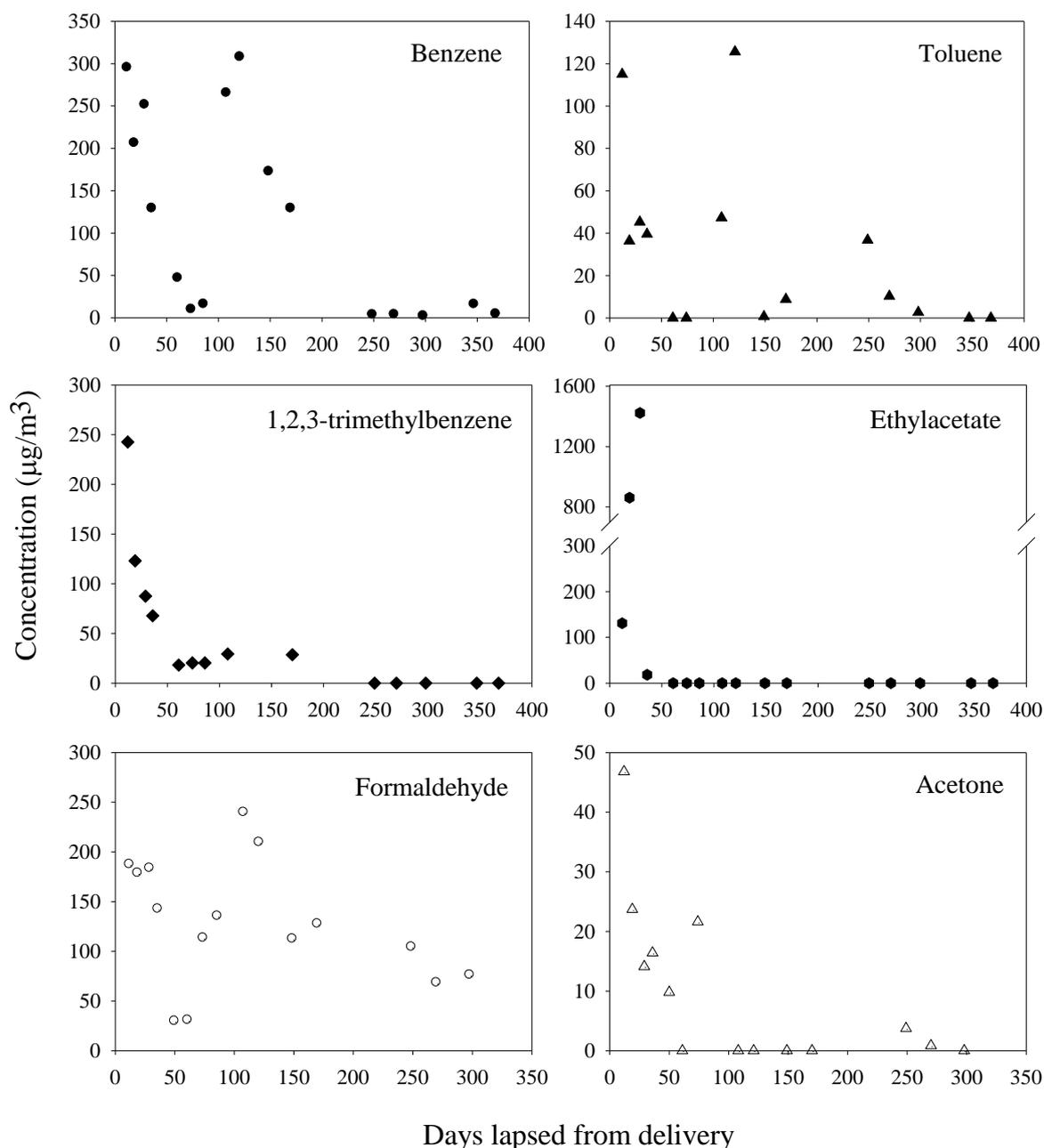


Figure 1 Time-dependent concentrations of the target VOCs in a new car cabin

The major in-cabin sources of benzene, toluene, and 1,2,3-trimethylbenzene are likely to be solvents used in paints, coatings, adhesives, degreasers, etc [11]. Figure 1 also reveals that the concentrations of benzene, toluene, and 1,2,3-trimethylbenzene decreased toward below the detection limits after six months. However, benzene and toluene levels exhibited two peak concentrations over the monitoring period. The second peak was possibly attributed to solvent evaporation from the newly replaced

rubber carpets before the sampling date of the 108th day. Surprisingly, ethyl acetate was measured at the highest concentration during the first month, but dramatically dropped to below the detection limit after that initial period. Ethyl acetate is used as a solvent for lacquers, enamel coatings, plastics, and electrostatic spray coatings for automobiles [12]. Levels of acetone, widely used as a solvent, decreased from ~50 µg/m³ at first sampling to below the detection limit after

two months. Formaldehyde concentration was measured at levels of 140-190 $\mu\text{g}/\text{m}^3$ in the first month, gradually decreasing over 5 months from delivery. However, formaldehyde concentrations remained relatively high at an average of 72 $\mu\text{g}/\text{m}^3$ by the end of the 10-month sampling course. To interpret the significance of health concerns, the in-cabin VOCs measured in this study were compared with the indoor concentration guidelines for non-industrial places formulated by the Ministry of Health, Labor and Welfare of Japan [13] based on concerns over sick building syndrome (SBS). Formaldehyde and toluene are the only two compounds listed in these guidelines for the 13 target VOCs. The in-cabin formaldehyde exceeded the guideline maximum of 100 $\mu\text{g}/\text{m}^3$ during the examination period for the first eight months, while the toluene levels did not exceed the guideline maximum of 260 $\mu\text{g}/\text{m}^3$.

Zhang et al. [11] measured VOCs in the cabins of 802 new cars parked in two parking garages in Beijing, China. The mean concentrations of benzene, toluene, and formaldehyde were reported as 0.27, 1.22, and 0.09 mg/m^3 , respectively. Benzene and formaldehyde concentrations were of the same order of magnitude as those measured in current study, whilst toluene levels were 10 times higher in the study of Zhang's group. The researchers attributed the high concentrations of toluene to the solvents and surface coatings in interior-car decoration.

2) Effect of in-cabin temperature on VOC concentrations

The Pearson test was used to determine linear association between the in-cabin temperature and concentrations of the six VOCs measured during the first five-months of the

sampling period. Table 2 shows the Pearson correlations (r) and their significance levels.

The Pearson test showed that only association between the in-cabin temperature and formaldehyde concentration was significant at the $p=0.05$ level while the other VOCs showed no statistically significant association. The reason is possibly due to the rapid depletion of the VOCs from the interior materials, resulting in a substantial decrease in their concentrations during the early part of monitoring period. However, a positive correlation was found between the formaldehyde concentrations and the in-cabin temperature (Figure 2), with formaldehyde concentrations increasing with temperature. The regression equation is shown below:

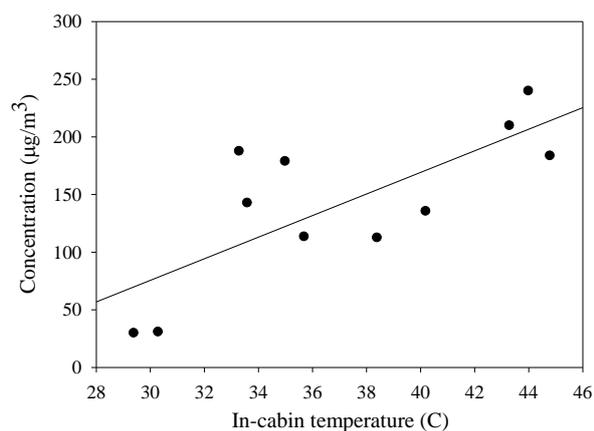
$$y = 9.38x - 206 \quad (1)$$

where x is the in-cabin temperature ($^{\circ}\text{C}$) and y is the formaldehyde concentration ($\mu\text{g}/\text{m}^3$).

However, the association analysis between the temperature and formaldehyde concentration during an entire sampling period of ten months showed no significance ($p=0.150$). The formaldehyde emission rate that is attributed to evaporative mass transfer from the surface of the interior materials and to desorption may decrease significantly after five months receiving delivery from the automobile factory. The major source of formaldehyde is likely to be formaldehyde-based adhesives such as urea-formaldehyde resin or phenol-formaldehyde resin [14], with emissions strongly dependent on ambient temperature. The other important sources of in-cabin formaldehyde were ozone reactions with organic compounds at the interface of interior surfaces and coatings, which can produce secondary organic pollutants such as carbonyls which include formaldehyde [15].

Table 2 Pearson correlations between the in-cabin temperature and VOC concentrations

VOCs	Pearson correlation	Significance level
Benzene	0.445	0.198
Toluene	0.302	0.430
1,2,3-Trimethylbenzene	-0.222	0.596
Ethyl acetate	0.300	0.400
Formaldehyde	0.750	0.008
Acetone	-0.697	0.054

**Figure 2** Relationship between in-cabin temperature and formaldehyde concentration

The ozone reactions that occur in the car cabin are of increasing concern particularly when the outdoor ozone levels are elevated, e.g. in the afternoons under conditions of strong solar radiation [16]. The elevated outdoor ozone levels attributed to atmospheric photochemistry can lead to increased levels of in-cabin ozone due to infiltration. The ozone-initiated reactions may result in persistency of formaldehyde detected in the cabin of the new car.

Conclusions

Levels of in-cabin VOCs for the new car were found to be high for the first month after delivery from the manufacturer, with concentrations tending to decline to below the respective detection limits during the monitoring period. However, the formaldehyde levels remained as high as $72 \mu\text{g}/\text{m}^3$ at the end of the 10-month sampling period, and were also found to be related to in-cabin temperature at a significance level of $p=0.05$. To promote healthy vehicle indoor air quality,

sources of in-cabin pollutants should be eliminated, e.g. by use of low-VOC emission materials and coatings. In addition to the source control, avoidance of pollutant sources such as air-fresheners or ozone-generating air-cleaning devices in the car cabin can minimize passenger exposure to in-cabin VOCs [17].

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