



# Health risk assessment and personal exposure to Volatile Organic Compounds (VOCs) in metro carriages – A case study in Shanghai, China



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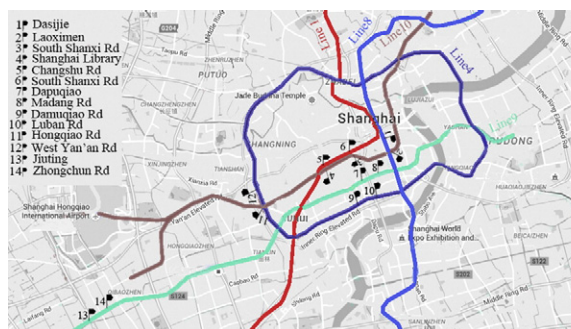
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## HIGHLIGHTS

- The VOCs concentration in different metro carriages under different route conditions were analyzed.
- The VOCs exposure levels inside metro carriages in Shanghai, China were calculated.
- The health risk of commuters' exposure to VOCs inside subway was estimated.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Air pollution in transportation cabins has recently become a public concern. However, few studies assessed the exposure levels of suspected air pollutants including Volatile Organic Compounds (VOCs). This paper studied the exposure levels of in-carriage VOCs (benzene, toluene, ethylbenzene, xylene, styrene, formaldehyde, acetaldehyde, acetone and acrolein) in Shanghai, China and estimated the health risk in different conditions. The results indicated that VOCs concentrations in metro carriages varied from different train models, due to the difference in carriage size and ventilation system. The concentrations of aromatic VOCs in old metro carriage were 1–2 times higher than the new ones, as better paintings were used in new trains. Poor air circulation and ventilation in the underground track was likely to be the cause of higher VOCs levels (~10%) than the above-ground track. Lower aromatic compounds levels and higher carbonyls levels were observed in metro carriages at suburban areas than those at urban areas, likely due to less aromatic emission sources and more carbonyls emission sources in suburban areas. Acetone and acrolein were found to increase from 7.71 to 26.28  $\mu\text{g}/\text{m}^3$  with number of commuters increasing from 40 to 200 in the carriages. According to the acceptable level proposed by the World Health Organization ( $1 \times 10^{-6}$ – $1 \times 10^{-5}$ ), the life carcinogenic risk of commuters by subway ( $8.5 \times 10^{-6}$ – $4.8 \times 10^{-5}$ ) was little above the acceptable level in Shanghai. Further application of our findings is possible to act as a reference in facilitating regulations for metro systems in other cities around world, so that in-carriage air quality might be improved.

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## 1. Introduction

Exposure to Volatile Organic Compounds (VOCs) such as formaldehyde and benzene can cause negative health effects (Tagiyeva and

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Sheikh, 2014). For instance, formaldehyde inhalation could exacerbate asthma symptoms (Casset et al., 2005) while exposure dosage to benzene is closely linked to childhood leukemia (Zhou et al., 2014). Potential sources of VOCs include material decoration, painting and surface coating. Particularly, VOCs determine indoor air quality and substantially threat human health as people in average spend 90% their time inside buildings or other man-made environments. With rapid development of subway transportation systems, the number of subway commuters has continuously increased over recent years in metropolitan cities (Prud'Homme et al., 2012). For example, Shanghai, as a prosperous and densely populated city, has one of the largest urban metro traffic systems in the world. Daily ridership averaged 8 million in 2014 and reached a record of about 10.3 million on April 30, 2015. Meanwhile, air quality in metro carriages is of great concern to the public as many atmospheric pollutants including VOCs in metro carriages have emerged, with their sources ranging from interior materials (Brodzik et al., 2014), passengers' breath (Zhao et al., 2016), to outdoor air infiltration. Thus, commuters' exposure to VOCs in metro carriages may cause perceivable health issues and risk as reported by many environmental health studies (e.g. Pang and Mu, 2007; Shiohara et al., 2005). It was estimated that the cancer risks from formaldehyde and acetaldehyde in metro carriages in Shanghai were approximately  $3.2 \times 10^{-4}$  and  $3.7 \times 10^{-5}$ , respectively (Feng et al., 2010). The Lifetime Carcinogenic Risk (LCR) from commuting by metro in Mexico City was estimated to be  $1.3 \times 10^{-5}$  to  $1.7 \times 10^{-5}$  based on the exposure to benzene and formaldehyde without considering other carcinogenic substances, such as acetaldehyde (Shiohara et al., 2005).

Previous studies in transportation microenvironment primarily focused on thermal conditions (Katavoutas et al., 2016), particulate matter (Kam et al., 2011; Kwon et al., 2015; Martins et al., 2016; Xu et al., 2016; Yu et al., 2012), airborne bacteria (Wang et al., 2010), PAHs

(Yan et al., 2015) and VOCs (Do et al., 2014; Kim et al., 2016). Many studies indicated that the VOCs levels in metro carriages were lower than those in roadway ones (Gómez-Perales et al., 2007; Chan et al., 2003; Lau and Chan, 2003; Pang and Mu, 2007). Factors may affect VOCs exposure levels in metro carriages including service time of metro trains, passenger numbers and driving conditions (Lau and Chan, 2003). However, to our knowledge, few studies have systematically assessed the effects of these factors on the VOCs levels. Furthermore, most of the previous studies only chose a single metro line from the beginning to the terminal station and lacked comprehensively presentation of VOCs exposure levels and its risk to human health in the entire metro system.

In this study, the concentrations of nine typical VOCs in the metro carriage were measured including benzene, toluene, ethylbenzene, xylene (BTEX), styrene, formaldehyde, acetaldehyde, acetone, and acrolein, which are currently regulated by Chinese National Standard of In-Cabin Air Quality under different driving scenarios. Then, the influence from some key factors (i.e., train model, service time, number of passengers, underground/above-ground, and urban/suburban areas) on in-carriage VOCs exposure levels were investigated. Finally, the health risk of various VOCs exposure scenarios was estimated to facilitate the risk-based regulatory decision making and formulation of mitigation measures for better protection of the public in metropolitan cities.

## 2. Methodology

### 2.1. Field study design

Five metro lines (Line 1, 4, 8, 9 and 10) in Shanghai were monitored for this study (Fig. 1). These five metro lines and other three lines (Line 2, Line 3, Line 7) constitute approximately 70% of the metro traffic

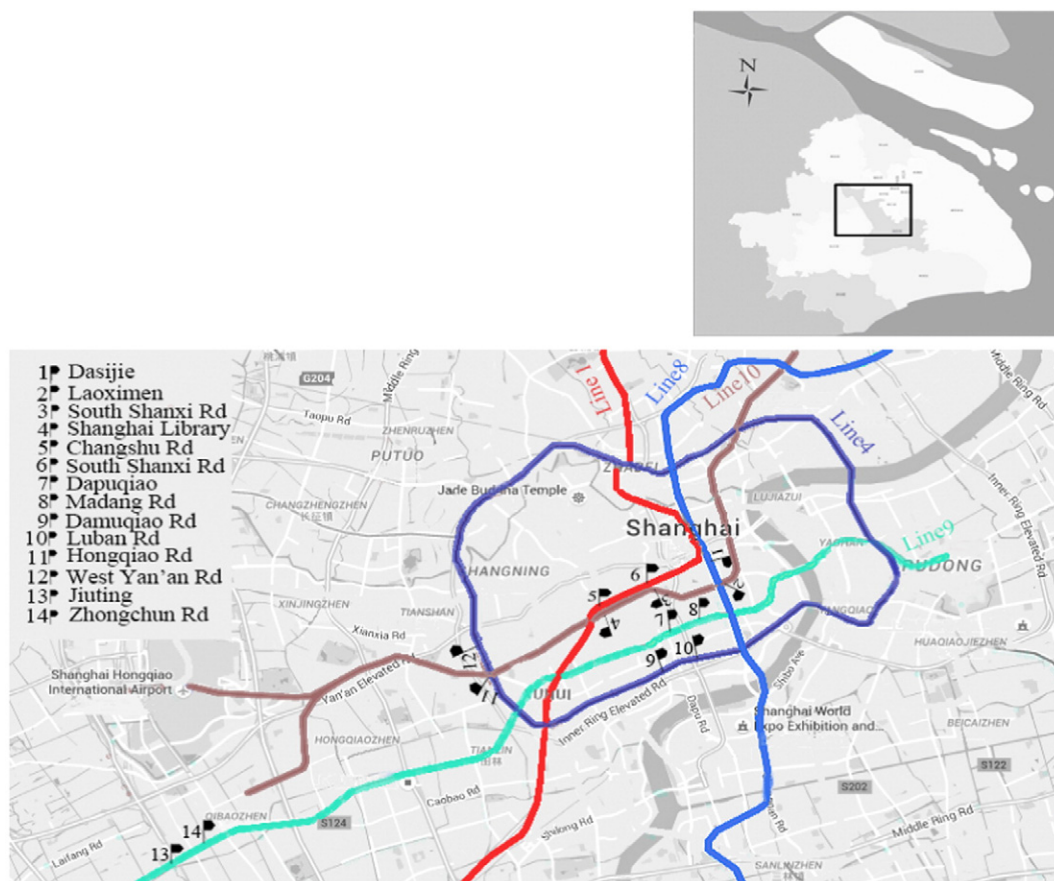


Fig. 1. Location of the sampling routes.

**Table 1**  
Information about the selected lines and sample routes.

Sample line	Model	Begin to service (year)	Urban or suburban	Underground or above-ground	Number of passenger
Line 1	B	1993	Urban	Underground	76
Line 4	B	2002	Urban	Underground	57
	B	2002	Urban	Above-ground	50
Line 8	A	2006	Urban	Underground	120
Line 9	B	2008	Urban	Underground	165
	B	2008	Suburban	Underground	172
Line 10	B	2010	Urban	Underground	40/60/90/150/200

system in Shanghai. The main characteristics of those lines are summarized in Table 1. The selected lines were used to investigate the effects of five factors on the concentrations of 9 VOCs in metro carriages, including (1) different train models, (2) service years of the train, (3) number of passengers, (4) ground or underground tracks, (5) urban or suburban areas. The train model on Line 8 (denoted model A) is 19.5 m in length, 2.6 m in width and 2.1 m in height. The ventilation supply airflow rate is 8000 m<sup>3</sup>/h with 20% of the total circulated air replaced by fresh air out of the cabins. All other lines are categorized as model B, which is 22.1 m in length, 3 m in width and 2.1 m in height. The ventilation supply airflow rate is 10,000 m<sup>3</sup>/h with 32% of the total circulated air replaced by fresh air out of the cabins. In addition, air conditioning in all metro trains in this study used air drawn from outside by fans. Line 1, which is the earliest line in service was compared with the relatively later one (Line 10) in the same district. We measured in-carriage VOCs in Line 10 in the presence of different numbers of passengers, i.e. 40, 60, 90, 150 and 200. Line 4 covers both underground and above-ground tracks. Line 9 runs in both urban and suburban areas. All of the metro lines in this study are equipped with Platform Screen Door systems. Air samples were collected during 8:00–10:00 a.m. on sunny days (usually 3 days per week when weather permitted) from Mar. 28 to Oct. 20, 2015 at the respiratory level in the middle of the train carriage. Portable air samplers, 6-L teflon sampling bags (E-Switch Inc., China) were used to collect samples after entering the metro train. Three sets of VOC samples were collected in duplicates for each trip during ventilation operation. Total VOC or TVOC, CO<sub>2</sub>, CO, temperature, relative humidity, barometric pressure, sampling time, travelling routes and number of passengers were recorded.

## 2.2. Sampling method and quality assurance

To collect the in-carriage VOC samples by 6-L teflon sampling bags, portable pumps (TWA-300XB, XBCY Inc. China) and stainless steel tubes filled with Tenax TA (N9307005, PerkinElmer Inc., US) were

used for sampling of benzene, toluene, ethylbenzene, xylene and styrene. Before sampling, all the Tenax TA tubes were conditioned in helium for 2 h at 225 °C. Another portable pump and 2,4-dinitrophenylhydrazine (DNPH) cartridge (Anpel Inc., China) were used for sampling formaldehyde, acetaldehyde, acetone and acrolein. Ozone scrubbers (Anpel Inc., China) were used as a pre-cartridge of XPOsure to minimize ozone interference. Flow rates of the pump were set at 0.2 L/min for aromatic VOCs and 0.4 l/min for carbonyl compounds, as calibrated by a gas flow meter (Model 4050, TSI Inc., USA). The sampling volume was calculated using the following equation:

$$V_s = Q_a t \times \frac{293.15}{273.15 + T} \times \frac{P}{101.325} \quad (1)$$

where  $V_s$  is the standard sampling volume (L);  $Q_a$  is the actual flow rate (litres/min) measured by the volume meter;  $t$  is the sampling time (min);  $T$  and  $P$  are the ambient temperature (°C) and the barometric pressure (kPa), respectively.

The analysis of the aromatic VOC samples from adsorbent tubes was performed by thermal desorption (TurboMatrix 350 ATD, Perkin-Elmer Inc., US) and gas chromatography/mass spectrometry (GC/MS) (GC/MS, DSQ-II, Thermo Fisher, US). A DB-5MS capillary column (30 m × 0.25 mm × 0.25 μm, Agilent Inc., US) was used on the GC and helium was used as the carrier gas. The oven temperature of the GC was initially held at 40 °C for 3 min and then raised to 60 °C at 2 °C/min and to 250 °C at 20 °C/min and kept for 3 min finally. The mass spectrometer was operated in the electron impact mode (70 eV) by a full scanning between 35 and 350 mass units.

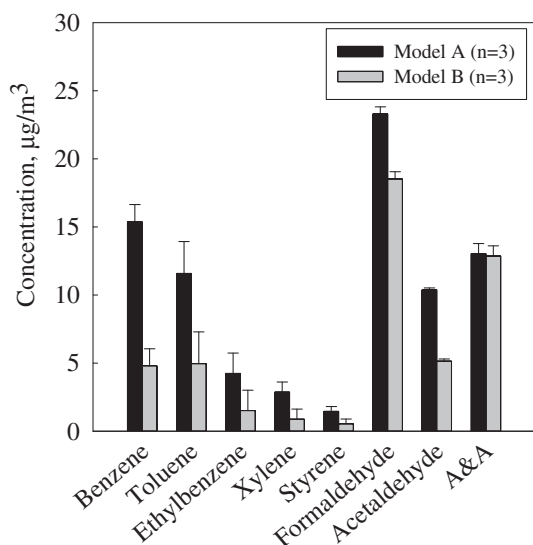
For the analysis of carbonyl compounds, the sampled cartridges were eluted by 5.0 mL acetonitrile and analyzed by a High-performance liquid chromatography (HPLC) system (1200-DAD, Agilent Inc., US). The analytical conditions were as follows: Athena C18-WP column (3 μm, 250 × 4.6 mm, CNW); mobile phase: 60% acetonitrile (HPLC gradient grade, Sinoreagent Inc., China) and 40% Milli-Q water; mobile-phase flow rate: 1.0 mL/min; injection volume: 25 μL; detector: UV at 360 nm.

Details of standard curve method, the equations and correlation coefficients ( $R^2$ ) of standard curves for benzene, toluene, ethylbenzene, xylene, styrene, formaldehyde, acetaldehyde, acetone and acrolein were in supporting information (Text S1 and Table S1). Five sets of duplicate VOC samples were collected to check the precision and reliability of the sampling and analytical method. The relative mean deviation of all duplicates was within 18% for the target compounds. At a signal-to-noise ratio of 3:1, the method detection limit (MDL) of all measured VOCs was below 0.5 μg/m<sup>3</sup>. Other common quality controls such as field blank check were also included.

**Table 2**  
The VOC levels in different metro lines.

Characteristics of lines	Mean concentration ± S.D. (μg/m <sup>3</sup> )							
	Line 1 (n = 3)		Line 4 (n = 6)		Line 8 (n = 3)	Line 9 (n = 6)		Line 10 (n = 21)
	Old	Underground	Above-ground	Model A	Urban	Suburban	New & model B	
Benzene	15.44 ± 2.96	27.50 ± 0.64	33.48 ± 1.96	15.25 ± 0.21	5.44 ± 0.13	5.30 ± 0.12	4.67 ± 0.53	
Toluene	12.06 ± 1.50	49.72 ± 4.5	62.47 ± 1.47	11.49 ± 0.56	9.09 ± 1.13	7.06 ± 0.78	5.22 ± 0.36	
Ethylbenzene	3.56 ± 0.47	8.65 ± 0.05	10.16 ± 0.47	4.21 ± 0.26	2.41 ± 0.09	1.84 ± 0.10	1.16 ± 0.27	
Xylene	3.45 ± 0.24	6.29 ± 0.45	10.29 ± 0.22	2.19 ± 0.19	2.45 ± 0.59	1.56 ± 0.14	1.06 ± 0.35	
Styrene	0.94 ± 0.06	3.79 ± 0.39	3.49 ± 0.15	1.44 ± 0.34	1.06 ± 0.57	0.83 ± 0.54	0.44 ± 0.15	
Formaldehyde	19.85 ± 0.33	10.19 ± 1.74	11.11 ± 1.99	23.30 ± 1.32	4.47 ± 0.49	12.02 ± 2.11	18.47 ± 2.39	
Acetaldehyde	10.31 ± 1.81	3.83 ± 0.05	4.66 ± 0.23	10.37 ± 0.39	0.39 ± 0.05	1.84 ± 0.28	5.49 ± 1.18	
Acetone and Acrolein	8.37 ± 0.44	8.29 ± 0.04	8.22 ± 0.24	13.04 ± 0.86	4.65 ± 0.73	11.24 ± 0.28	15.66 ± 7.84	
Total VOCs	89.90 ± 8.45	118.27 ± 4.35	143.89 ± 2.98	99.21 ± 3.6	29.97 ± 2.33	41.70 ± 3.91	68.10 ± 9.55	

n: the number of samples.

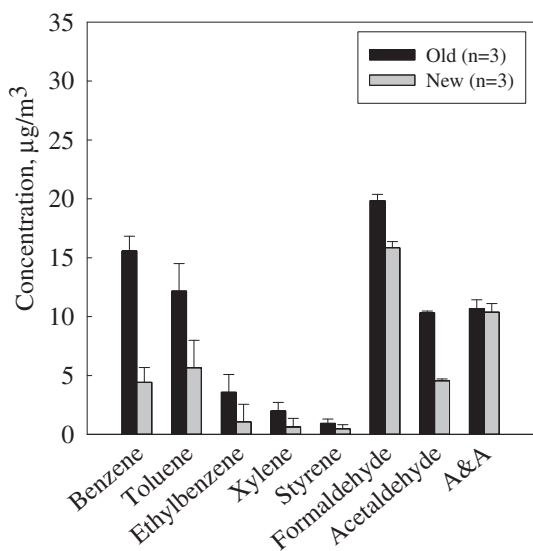


**Fig. 2.** Mean concentrations of VOCs in metro carriages of different models from 8:00 to 10:00 a.m. A&A: Acetone and Acrolein. The error bar represents the value of standard deviation.

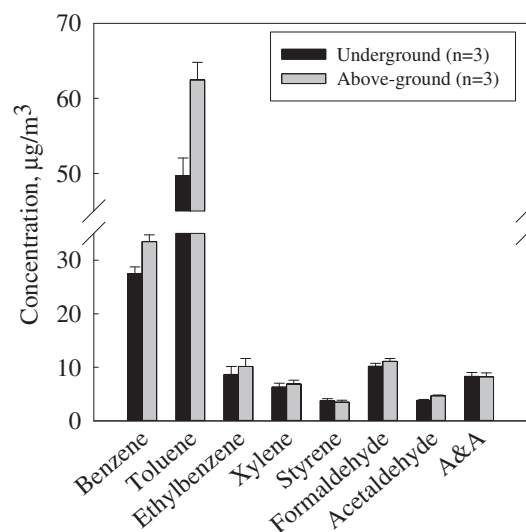
### 3. Results and discussion

#### 3.1. Levels of VOCs exposure in metro carriages

During the sampling period, a total of 78 samples were collected in five metro lines with 39 samples for aromatic VOCs analysis and the other 39 samples for carbonyls analysis. The VOCs concentrations in different lines are listed in Table 2. The highest total VOCs exposure level occurred in Line 4 under above-ground route condition ( $143.89 \pm 2.98 \mu\text{g}/\text{m}^3$ ), whereas the lowest level was observed in Line 9 at urban area ( $29.97 \pm 2.33 \mu\text{g}/\text{m}^3$ ). The total VOCs exposure level in the carriage of model A metro train ( $99.21 \pm 3.6 \mu\text{g}/\text{m}^3$ ) was higher than that in the carriage of model B metro train ( $68.10 \pm 9.55 \mu\text{g}/\text{m}^3$ ). The total VOCs exposure level in old metro carriage ( $89.90 \pm 8.45 \mu\text{g}/\text{m}^3$ ) was higher than that in new metro carriage ( $68.10 \pm 9.55 \mu\text{g}/\text{m}^3$ ). Compared with underground route condition ( $118.27 \pm 4.35 \mu\text{g}/\text{m}^3$ ), the total

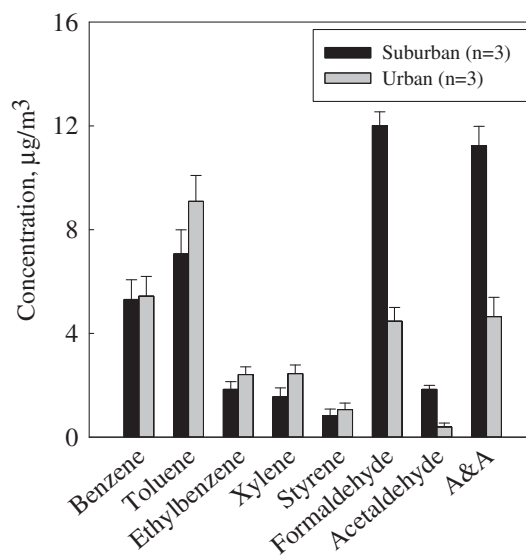


**Fig. 3.** Mean concentrations of VOCs in new and old metro carriages from 8:00 to 10:00 a.m. A&A: Acetone and Acrolein. The error bar represents the value of standard deviation.

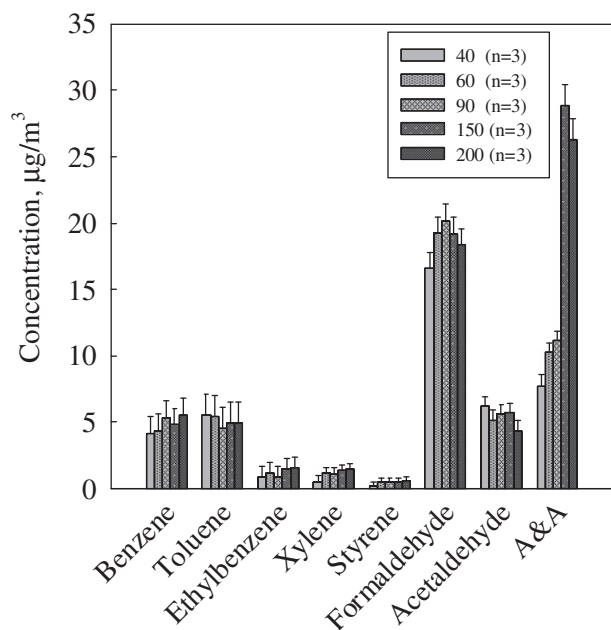


**Fig. 4.** Mean concentrations of VOCs in metro carriages of underground and above-ground from 8:00 to 10:00 a.m. A&A: Acetone and Acrolein. The error bar represents the value of standard deviation.

VOCs concentrations in metro carriage were higher under above-ground route condition. The total VOCs concentrations in metro carriage at suburban areas were higher ( $41.70 \pm 3.91 \mu\text{g}/\text{m}^3$ ) than that at urban areas ( $29.97 \pm 2.33 \mu\text{g}/\text{m}^3$ ). Among the aromatic VOCs, toluene and benzene were the two compounds with largest average concentrations ( $14.25$  and  $18.60 \mu\text{g}/\text{m}^3$  respectively) in all metro lines. The benzene level in Line 4 was the highest ( $33.48 \pm 1.96 \mu\text{g}/\text{m}^3$  for above-ground route condition and  $27.50 \pm 1.26 \mu\text{g}/\text{m}^3$  for underground route condition), followed by Line 1 ( $15.44 \pm 2.96 \mu\text{g}/\text{m}^3$ ), Line 8 ( $15.25 \pm 0.21 \mu\text{g}/\text{m}^3$ ), Line 9 ( $5.44 \pm 0.13 \mu\text{g}/\text{m}^3$  for urban area and  $5.30 \pm 0.12 \mu\text{g}/\text{m}^3$  for suburban area) and Line 10 ( $4.67 \pm 0.53 \mu\text{g}/\text{m}^3$ ). The variations of the other four aromatic compounds were similar with benzene. The concentration of aromatic VOCs in Line 1 was higher than that in Line 9 and 10, because the air filter used in Line 1 was coarse stainless steel wire mesh or aluminium mesh which may not effectively stop VOCs from entering the carriage. The concentration of aromatic VOCs in Line 8 was also higher than that in Line 9 and 10, primarily



**Fig. 5.** Mean concentrations of VOCs in metro carriages of urban and suburban area from 8:00 to 10:00 a.m. A&A: Acetone and Acrolein. The error bar represents the value of standard deviation.



**Fig. 6.** Mean concentrations of VOCs in metro carriages with different passenger numbers from 8:00 to 10:00 a.m. A&A: Acetone and Acrolein. The error bar represents the value of standard deviation.

due to the differences in carriage size and ventilation conditions. The metro train of Line 8 has much higher S/V (interior superficial area/volume) and lower fresh air ratio than other metro trains. The aromatic VOCs levels in Line 9 were close to that in Line 10, which was ascribed to their same model of metro train (model B), similar service years (6–8 years) and same routes condition (underground). On the other hand, the total concentrations of measured carbonyls were  $46.71 \pm 3.15$ ,  $39.62 \pm 8.06$ ,  $38.53 \pm 2.08$ ,  $25.10 \pm 1.48$ ,  $23.99 \pm 0.74$ ,  $22.31 \pm 1.13$  and  $9.51 \pm 1.04 \mu\text{g}/\text{m}^3$  for Line 8, 10, 1, 9 (suburban), 4 (above-ground), 4 (underground) and 9 (urban), respectively. For carbonyl compounds, the highest concentration was observed for formaldehyde ranging from  $4.47$  to  $23.3 \mu\text{g}/\text{m}^3$ . Compared with other lines in this study, the concentration of acetone and acrolein was the highest in Line 10. This was due to the large number of passengers in Line 10 during the sampling period, which could be the large source of acetone (Miekisch et al., 2004).

The above results indicated that the VOCs exposure levels varied with the different metro carriages and different driving conditions. Shanghai metro trains can be categorized into two models (A and B) according to their carriage sizes (width, length, and height) and fresh air ratios (the outside airflow rate/the total supply airflow rate). The VOCs concentrations Line 8 (model A) and Line 10 (model B) are compared in Fig. 2. Model A train seems to present consistently greater VOCs (benzene, toluene, ethylbenzene, xylene, formaldehyde, acetaldehyde) concentrations than model B train ( $P < 0.05$ , *t*-test), due to the

differences in carriage size and ventilation conditions. For instance, Model A train has much higher S/V (interior superficial area/volume) than model B. Furthermore, the fresh air ratio of model A metro train is lower than that of model B. Therefore, VOCs from interior decoration emissions (e.g. painting and surface coating) could accumulate more easily in Line 8 than Line 10. Meanwhile, the concentrations of benzene, toluene, xylene, ethylbenzene, styrene, formaldehyde and acetaldehyde were larger inside the old metro train (Line 1) than in the new train (Line 10) by about one to two times as shown in Fig. 3 ( $P < 0.05$ , *t*-test), owing to the improvement of paintings used (e.g., water-borne paints in new trains versus solvent-borne paints in old trains). Another potential explanation is that the air filter used in the ventilation system of old metro train is coarse stainless steel wire mesh or aluminium mesh that cannot effectively prevent VOCs from entering the carriage, while the new metro trains are equipped with fibrous air filter with higher filtration efficiency. Fig. 4 shows that the VOCs (benzene, toluene, ethylbenzene, xylene, formaldehyde, acetaldehyde) levels in the underground track were 10% less than those the above-ground track in the same metro train (Line 4) ( $P < 0.05$ , *t*-test), which was consistent with previously results reported by Lau and Chan (2003). This was probably attributed to the fact that under underground condition, the VOCs in metro carriage was less influenced by vehicular emission on the street.

Lower aromatic compounds levels and higher carbonyls levels were observed inside metro carriages driving at suburban area as opposed to urban area (Fig. 5;  $P < 0.05$ , *t*-test). This is probably because of the heavy traffic in urban areas of Shanghai that emits VOCs. However, the relatively high levels of formaldehyde, acetaldehyde, acetone and acrolein in metro carriage at suburban areas may come from other emission sources, such as chemical factories at Caohejing Industrial Zone, which is about 5.5 km away from the sampling site (Ho et al., 2013). This result was consistent with previous study (Lau and Chan, 2003), which indicated that for the railway transport, in-vehicle aromatic VOCs were approximately 2–3 times higher at urban areas than suburban areas.

The dependence of VOC levels on passenger numbers was shown in Fig. 6. Most VOCs did not change significantly with the number of commuters, acetone and acrolein increased from  $7.71$  and  $26.28 \mu\text{g}/\text{m}^3$  as the commuters' number increased from 40 to about 200 in metro carriages ( $P = 0.004$ , one-way ANOVA). Similar results could also be found in previous study (Pang and Mu, 2007), in which acetone concentrations were enhanced from  $12.3 \pm 4.6 \mu\text{g}/\text{m}^3$  to  $21.6 \pm 5.9 \mu\text{g}/\text{m}^3$  with increasing commuter number from several to about 300 in a subway cabin. It was believed that acetone was excreted from human metabolism (Miekisch et al., 2004). Therefore, acetone and acrolein were not well correlated with other measured VOCs ( $R < 0.44$ ) as shown in Table 3. By contrast, the five target aromatic VOCs had good correlations ( $R > 0.94$ ), indicating that the in-carriage aromatic VOCs were mainly from the same sources (e.g., motor vehicles emission) on metro carriages. This was consistent with the result in study on other transportations (Li et al., 2009), which found that aromatic compounds in bus had strong correlations and vehicle emission was the main source. On the other hand, formaldehyde and acetaldehyde were well correlated ( $R > 0.79$ ). The correlations between carbonyls (formaldehyde, acetaldehyde, acetone and

**Table 3**  
Correlation coefficients for VOCs measured in metro carriages in Shanghai.

	Benzene	Toluene	Ethylbenzene	Xylene	Styrene	Formaldehyde	Acetaldehyde	A&A
Benzene	1							
Toluene	0.957**	1						
Ethylbenzene	0.988**	0.977**	1					
Xylene	0.964**	0.965**	0.990**	1				
Styrene	0.948**	0.966**	0.979**	0.980**	1			
Formaldehyde	0.307	0.473	0.421	0.522	0.491	1		
Acetaldehyde	0.143	0.105	0.010	0.091	0.114	0.794*	1	
Acetone and Acrolein	0.332	0.334	0.320	0.377	0.323	0.440	0.105	1

\*  $P < 0.05$ .

\*\*  $P < 0.001$ .

**Table 4**  
Personal exposure risks of VOCs in metro carriages of different conditions.

Line of subway		Line 1	Line 4		Line 8	Line 9	Line 10	
Characteristics of carriage and route conditions		Old	Underground	Above-ground	Model A	Urban	Suburban	New & model B
Benzene	Exposure( $\mu\text{g}/\text{day}$ )	19.45	34.64	42.19	19.22	6.85	6.69	5.89
	LCR	$2.0 \times 10^{-5}$	$3.5 \times 10^{-5}$	$4.3 \times 10^{-5}$	$2.0 \times 10^{-6}$	$7.0 \times 10^{-6}$	$6.8 \times 10^{-6}$	$6.0 \times 10^{-6}$
Ethylbenzene	Exposure( $\mu\text{g}/\text{day}$ )	4.48	10.90	12.80	5.30	3.04	2.32	1.46
	LCR	$4.0 \times 10^{-7}$	$9.7 \times 10^{-7}$	$1.1 \times 10^{-6}$	$4.7 \times 10^{-7}$	$2.7 \times 10^{-7}$	$2.1 \times 10^{-7}$	$1.3 \times 10^{-7}$
Styrene	Exposure( $\mu\text{g}/\text{day}$ )	1.18	4.78	4.40	1.81	1.34	1.04	0.55
	LCR	$6.9 \times 10^{-9}$	$2.8 \times 10^{-8}$	$2.6 \times 10^{-8}$	$1.1 \times 10^{-8}$	$7.8 \times 10^{-9}$	$6.1 \times 10^{-9}$	$3.2 \times 10^{-9}$
Formaldehyde	Exposure( $\mu\text{g}/\text{day}$ )	25.01	12.84	14.00	29.35	5.64	15.14	23.28
	LCR	$5.4 \times 10^{-6}$	$2.8 \times 10^{-6}$	$3.0 \times 10^{-6}$	$6.3 \times 10^{-6}$	$1.2 \times 10^{-6}$	$3.2 \times 10^{-6}$	$5.0 \times 10^{-6}$
Acetaldehyde	Exposure( $\mu\text{g}/\text{day}$ )	12.99	4.83	5.87	13.07	0.49	2.32	6.92
	LCR	$1.3 \times 10^{-6}$	$4.9 \times 10^{-7}$	$6.0 \times 10^{-7}$	$1.3 \times 10^{-6}$	$5.0 \times 10^{-8}$	$2.4 \times 10^{-7}$	$7.1 \times 10^{-7}$
All VOCs	Exposure( $\mu\text{g}/\text{day}$ )	63.11	68.00	79.26	68.75	17.35	27.51	38.09
	LCR	$2.7 \times 10^{-5}$	$3.9 \times 10^{-5}$	$4.8 \times 10^{-5}$	$2.8 \times 10^{-5}$	$8.5 \times 10^{-6}$	$1.1 \times 10^{-5}$	$1.2 \times 10^{-5}$

acrolein) and the aromatic VOCs were poor. Clearly, carbonyls and the aromatic VOCs may come from different sources. For example, the aromatic VOCs come from gasoline vapor and vehicle emission while formaldehyde in metro trains largely derives from photochemical reactions in the atmosphere (Shiohara et al., 2005). Considering Shanghai is one of the largest cities in China which has many industries in suburban areas, the source of carbonyls was most likely to be emissions from chemical factories and photochemical reactions (Cheng et al., 2014).

### 3.2. Exposure and health risk

The individual exposures and cancer risk to the VOCs in metro carriages were calculated by EPA (1992) and OEHHA (2003):

$$E_i = C_j \times IR_i \times t_{ij} \quad (2)$$

where  $E_i$  is the personal exposure to pollutant  $i$  ( $\text{mg}/\text{day}$ ),  $C$  is the concentration of the pollutant ( $\text{mg}/\text{m}^3$ ),  $IR$  is the inhalation rate ( $\text{m}^3/\text{h}$ ),  $t$  is the exposure time ( $\text{h}/\text{day}$ ), and  $j$  is the microenvironment.

The chronic daily intake (CDI,  $\text{mg}/\text{kg}/\text{day}$ ) attributable to inhalation was calculated as

$$CDI_i = \frac{E_i \times EF \times ED}{BM \times AL \times NY} \times 90\% \quad (3)$$

where  $CDI_i$  is the daily inhalation intake of pollutant  $i$  ( $\text{mg}/\text{kg}/\text{day}$ );  $EF$  the exposure frequency ( $\text{day}/\text{year}$ );  $ED$  the exposure duration (years), given as the working lifetime for adults;  $BM$  body mass ( $\text{kg}$ );  $AL$  the average lifetime (70 years);  $NY$  the number of days per year (365 days/year); and 90% the absorption factor of VOCs for humans (Colman Lerner et al., 2012).

Lifetime cancer risk (LCR) is the increased probability of developing cancer as a result of a specific exposure and was calculated by multiplying the intake of a toxic substance by the cancer potency factor, as follows:

$$LCR_i = CDI_i \times CPF_i \quad (4)$$

where  $LCR_i$  is the cancer risk associated with compound  $i$ ;  $CDI_i$  the daily intake of compound  $i$ ; and  $CPF_i$  represents the inhalation cancer potency factor of compound  $i$ . The cumulative cancer risks were determined by adding all the known, possible, and probable carcinogens (Payne-Sturges et al., 2004).

In this study, the VOCs inside five typical metro lines were selected to calculate the lifetime cancer risk (LCR). The results for personal exposure were estimated in different conditions to calculate the estimated health risk shown in Table 4. The LCR was slightly higher than the acceptable level proposed by the World Health Organization (WHO),

which was in the range of  $1 \times 10^{-6}$  to  $1 \times 10^{-5}$ . The highest value of LCR occurred in Line 4 under above-ground route condition ( $4.8 \times 10^{-5}$ ), whereas the lowest level was observed in Line 9 at urban area ( $8.5 \times 10^{-6}$ ). The LCR in old metro train was 2.1 times higher than new metro train, owing to the improved air filtration and painting material quality in new metro train. Compared with model A metro train, the LCR in model B is 2.3 times higher due to the high S/V (interior superficial area/volume) and low fresh air ratio in model B metro train. Under above-ground route condition, the LCR in metro carriage was 2.5% higher than that under underground route condition, where the VOCs in metro carriage received less input from vehicular emission on the street. Compared with urban areas, LCR in metro carriage at suburban areas was 29.4% higher, probably due to industrial activities as mentioned above. Moreover, the exposures of the current study were calculated only based on the 2 h of mean exposure time for the commuters. Given longer exposure time, e.g. subway drivers, the personal exposures would be three or four times higher than the current level.

### 4. Conclusions

This study measured the exposure levels and evaluated health risk of VOCs in different metro carriages under different driving conditions in Shanghai, China. The exposure levels were greatly influenced by the characteristics of metro carriages and driving conditions. The VOCs concentrations and health risk in metro carriages of Line 8 (model A) were significantly higher than Line 10 (model B). This difference was due to the higher S/V (interior superficial area/volume) and lower fresh air ratio in model A. Compared with new metro carriage (Line 10), the concentrations of VOCs and LCR inside old metro carriage (Line 1) were larger. The VOCs levels and exposure risk in the underground track were slightly lower than the above-ground track in the same metro train (Line 4). Lower aromatic compounds levels and higher carbonyls levels were observed inside metro carriages at suburban areas than at urban areas. In addition, we found that the acetone and acrolein were emitted not only from metro interior surfaces but also from the commuters in metro carriages. Good correlations were found between aromatic VOCs. Commuting via metro carriage presents low health risks from exposure to VOCs in metro carriages, which should be regulated in the long term to mitigate the risk.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.scitotenv.2016.08.072>.

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