



Rush-hour aromatic and chlorinated hydrocarbons in selected subway stations of Shanghai, China

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Abstract

Air samples were collected simultaneously at platform, mezzanine and outdoor in five typical stations of subway system in Shanghai, China using stainless steel canisters and analyzed by gas chromatography-mass selective detector (GC-MSD) after cryogenic pre-concentration. Benzene, toluene, ethylbenzene and xylenes (BTEX) at the platforms and mezzanines inside the stations averaged (10.3 ± 2.1), (38.7 ± 9.0), (19.4 ± 10.1) and (30.0 ± 11.1) $\mu\text{g}/\text{m}^3$, respectively; while trichloroethylene (TrCE), tetrachloroethylene (TeCE) and para-dichlorobenzene (pDCB), vinyl chloride and carbon tetrachloride were the most abundant chlorinated hydrocarbons inside the stations with average levels of (3.6 ± 1.3), (1.3 ± 0.5), (4.1 ± 1.1), (2.2 ± 1.1) and (1.2 ± 0.3) $\mu\text{g}/\text{m}^3$, respectively. Mean levels of major aromatic and chlorinated hydrocarbons were higher indoor (platforms and mezzanines) than outdoor with average indoor/outdoor (I/O) ratios of 1.1–9.5, whereas no significant indoor/outdoor differences were found except for benzene and TrCE. The highly significant mutual correlations ($p < 0.01$) for BTEX between indoor and outdoor and their significant correlation ($p < 0.05$) with methyl *tert*-butyl ether (MTBE), a marker of traffic-related emission without other indoor and outdoor sources, indicated that BTEX were introduced into the subway stations from indoor/outdoor air exchange and traffic emission should be their dominant source. TrCE and pDCB were mainly from indoor emission and TeCE might have both indoor emission sources and contribution from outdoor air, especially in the mezzanines.

Key words: subway; volatile organic compounds; aromatic hydrocarbons; chlorinated hydrocarbons; methyl *tert*-butyl ether; Shanghai

DOI: 10.1016/S1001-0742(11)60736-5

Introduction

Analysis of human exposures to volatile organic compounds (VOCs) is a key element of strategies designed to protect public health from the adverse effects of hazardous air pollutants (HAPs). In recent years, there is an increasing concern about people's exposure to HAPs in daily commuting trips (Chan et al., 2003; Lau and Chan, 2003; Sexton et al., 2004), particularly in rush hours when more citizens are exposed to elevated levels of traffic-related air pollutants (Cocheo et al., 2000). Exposure to VOCs, particularly those classified as known or suspected carcinogens, can pose potential adverse health effects. Benzene, for example, is a carcinogenic compound inducing leukemia. In addition, VOCs are important precursors of many secondary pollutants, which in turn cause the deterioration of air quality both outdoor and indoor (Odum et al., 1997).

As comfort inside transportation vehicles is important to passengers and subway is the most important mass transport mode in many modern mega cities, quite a lot studies

have been conducted on the levels of particulate matters, CO_2 and CO in subway systems (Chan et al., 2002a, 2002b; Gómez-Perales et al., 2004; Aarnio et al., 2005; Nieuwenhuijsen et al., 2007). However, studies on VOCs inside subway systems are comparatively quite limited. Only aromatic hydrocarbons inside subway networks have been measured and assessed in a few cities, such as Boston, USA (Chan et al., 1991), Paris, France (Dor et al., 1995), Berlin, Germany (Fromme et al., 1997), Mexico City, Mexico (Gómez-Perales et al., 2004; Shiohara et al., 2005) and Sao Paulo, Brazil (Fujii et al., 2007). In China, few reports for aromatic hydrocarbons inside subway carriages (Chan et al., 2003; Lau and Chan, 2003) and no reports are available in subway systems for some hazardous halocarbons widely detected in indoor environments (Pellizzari et al., 1986; Hartwell et al., 1992; Kostianen, 1995; Lee et al., 2002; Sexton et al., 2004; Sakai et al., 2004; Tang et al., 2005).

An apparent benefit of subway transport is that it will limit emission of hazardous air pollutants from vehicle exhaust through the reduction in automobile use. To keep pace with the rapid economic growth and urban expansion, public transportation system in China's large cities like

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Shanghai has been developing as a priority to relieve traffic jams. Shanghai, a mega city with an area of 6341 km² and a population over 18 million, is one of the most economically developed and densely populated cities in China. Subway has become the most important mass transportation mode in Shanghai with more than three million people per day using subway during rush hours. The passenger numbers showed an upward tendency with the construction of new lines and upgrade of current subway lines, and more importantly, with more people choose subway for local transport. Until 2010, Shanghai subway system has 11 lines and the total length of 424 km, becomes the second longest subway in the world (<http://www.shmetro.com/company/index.htm>).

VOCs inside subway systems would add passengers' exposure to hazardous air pollutants particularly for those commuting via subway between their working and dwelling places during rush-hours. On the other hand, when trains stop at the stations with doors open, VOCs inside subway carriages would have substantial contribution from those in the underground stations due to air exchange. Inside subway carriages, emission from indoor materials would decrease with time and contribute less and less to indoor VOCs, and air exchange with the stations would become increasingly important. Therefore, study of VOCs in subway stations in addition to those in subway carriages is also necessary for assessing VOCs' exposure inside subway systems. In this work, we aimed to investigate hazardous organic pollutants, including aromatic and chlorinated hydrocarbons, in the subway stations at rush hours in the Shanghai metropolitan area. Five stations were

selected for collecting whole air samples using canisters at the platforms, mezzanines and outdoor simultaneously. The purpose is to investigate exposure levels and possible sources of aromatic and chlorinated hydrocarbons inside the subway stations.

1 Methods

1.1 Sampling

Five typical subway stations, namely, Century Park (CP), Zhongshan Park (ZSP), Lujiazui (LJZ), Shanghai Railway (SRS) and Xujiahui (XJH), were selected for field measurements. Figure 1 shows locations of the five stations on line 1 and line 2. The two lines accounted for about 60% of the total passenger flow in the subway system. ZP is the transit station of lines 2, 3 and 4. SRS is the transit station of lines 1, 3 and 4. XJH station is the transit station of lines 1 and 9 and is also the largest station in Shanghai subway system with fourteen gates, some of which are directly open to multi-storey commercial/office buildings. There are much more passengers in these three stations than the other two stations, CP and LJZ, in the Pudong District far away from the old urban. In each station the mezzanine is the hall with ticket offices, check-in/out gates, small shops, food courts and multiple entrances/exits open either to the outside streets or to large commercial/office buildings. Unlike the mezzanines, there are no small shops or food courts in the platforms. Passengers need check-in at the mezzanine and walk downstairs to the platform to take the train.

The sampling campaign was conducted on July 25,

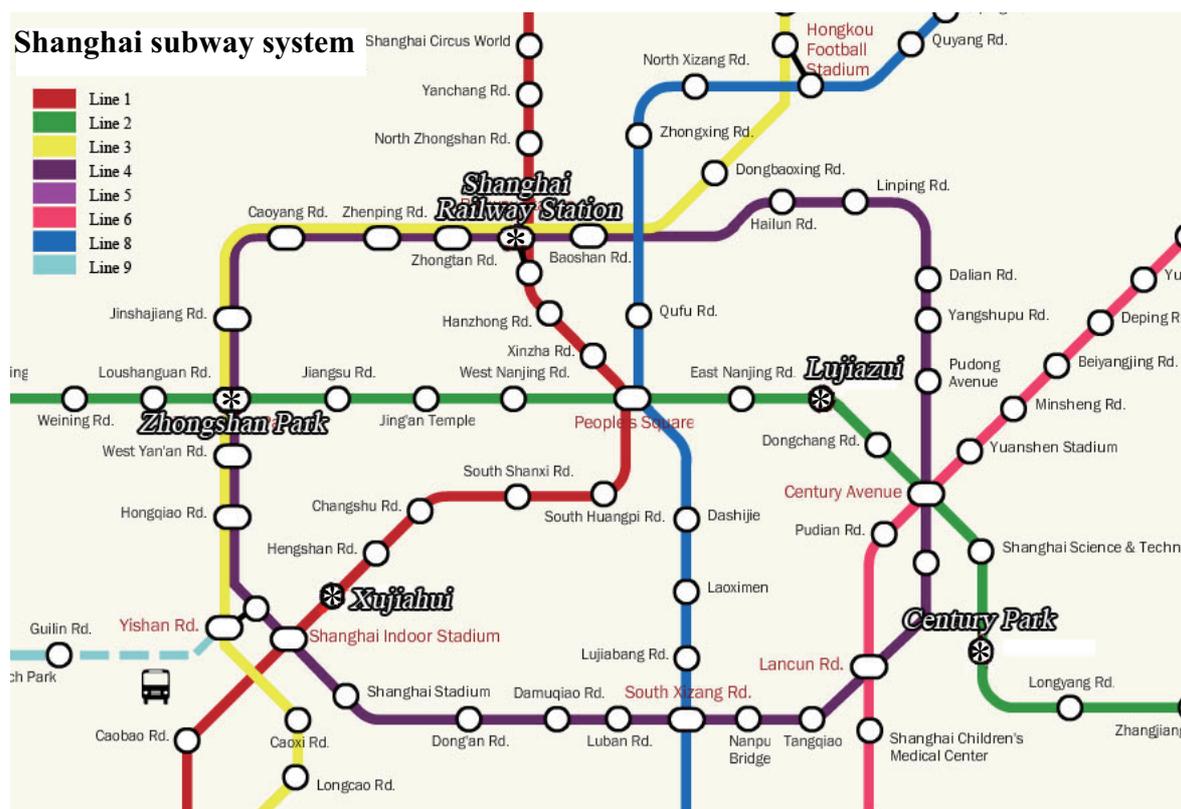


Fig. 1 Sketch map of Shanghai subway system (* indicates the stations where samples were collected).

2007. At each station, three sites, namely platform, mezzanine and outdoor, were selected for air sampling. The outdoor sampling site in a station was chosen to be near one gate open alongside the street. In the platform or mezzanine samples were collected in its central part. Whole air samples were taken at rush hours, namely, 7:00–9:00, 12:00–14:00, and 16:30–18:30, respectively. Air samples were collected using 2 L pre-evacuated stainless steel canisters. Before sampling, all canisters were cleaned and evacuated. During sampling an orifice flow regulator was connected to the canister to allow the canister to be filled in about 60 min. Total forty-five air samples were collected from the campaign. After sampling, all the canister samples were delivered to the laboratory for chemical analysis within a week.

1.2 Laboratory analysis of VOCs

The samples were analyzed using a Model 7100 preconcentrator (Entech Instruments Inc., USA) coupled with a gas chromatography-mass selective detector (GC-MSD, Agilent 5973N, USA). Detailed cryogenically concentration steps are described elsewhere (Yi et al., 2007; Wang and Wu, 2008; Zhang et al., 2010). Briefly, 500 mL air in each canister was drawn through a liquid-nitrogen cryogenic trap at -160°C to get VOCs trapped. The trapped VOCs were then transferred by pure helium to a secondary trap at -40°C with Tenax-TA as adsorbent. Majority of CO_2 was removed during this step. After that the secondary trap was heated to transfer target VOCs to a third cryofocus trap at -170°C . After the focusing step, the trap was rapidly heated and VOCs were transferred to the GC-MSD system. A HP-1 capillary column ($60\text{ m} \times 0.32\text{ mm} \times 1.0\text{ }\mu\text{m}$, Agilent Technologies, USA) was used with helium as carrier gas. The GC oven temperature was programmed to be initially at -50°C , holding for 3 min; increasing to 10°C at $15^{\circ}\text{C}/\text{min}$, then to 120°C at $5^{\circ}\text{C}/\text{min}$, then to 250°C at $10^{\circ}\text{C}/\text{min}$, and finally holding for 10 min. The MSD was used in selected ion monitoring (SIM) mode and the ionization method was electron impacting (EI).

1.3 Quality control and quality assurance

Before sampling, all canisters were cleaned at least five times by repeatedly filling and evacuating of humidified zero air. In order to check if there was any contamination in the canisters, all vacuumed canisters after cleaning procedure were re-filled with pure nitrogen and stored in the laboratory for at least 24 hr. Then the canisters were analyzed the same way as field samples to make sure that all the target VOCs were not present or below the method detection limits (MDLs).

Target compounds were identified based on their retention times and mass spectra, and quantified by multi-point external calibration method. The calibration standards were prepared by dynamically diluting the 100 ppbV TO-14 (39 compounds) and TO-15 (25 compounds) standard mixtures (Spectra Gases Inc., USA) to 0.5, 1, 5, 15 and 30 ppbV. The calibration curves were obtained by running the five diluted standards plus humidified zero air the same way as the field samples. The analytical

system was challenged daily with a one-point (typically 1 ppbV) calibration before running air samples. If the response was beyond $\pm 10\%$ of the initial calibration curve, recalibration was required. The method detection limits of target compounds in present study were all below $0.1\text{ }\mu\text{g}/\text{m}^3$.

1.4 Statistics methods

Statistical analysis of data was performed using SPSS 13.0 for windows. Means were compared by paired-samples *T*-test (2-tailed) for the significance levels. The calculation of Pearson correlation coefficients between species and tests of their significance (2-tailed) were also done using the SPSS software.

2 Results and discussion

In the present study, we mainly focused on two groups of toxic VOCs, namely, monocyclic aromatic hydrocarbons (AHs) and chlorinated hydrocarbons (CHs), which are classified as HAPs by US EPA. The means, mediums and ranges of indoor (platforms and mezzanines) and outdoor VOC concentrations are listed in Table 1, together with their cancer classification by the International Agency for Research on Cancer (IARC, 2004) and inhalation unit risk values (Caldwell et al., 1998; CalEPA, 2002). Some halocarbons, like CFC-11 and CFC-12, are not listed in Table 1 since these halocarbons in ambient air are not directly hazardous to human health although they are of concern due to their ozone depletion potentials and impacts on global environment. Also, those halocarbons with lower concentration levels ($< 1.0\text{ }\mu\text{g}/\text{m}^3$) were excluded in the present study.

2.1 Aromatic hydrocarbons

As an important class of air toxics with many anthropogenic emission sources, aromatic hydrocarbons are often present in the air with comparatively higher levels among VOCs, and are of priority in the survey of primary/secondary and indoor/outdoor air pollutants (Odum et al., 1997; Zhao et al., 2004). Many previous studies concerning exposure in transportation modes or in urban microenvironments have investigated aromatic hydrocarbons inside subway carriages (Chan et al., 1991, 2003; Dor et al., 1995; Fromme et al., 1997; Gomez-Perales et al., 2004; Lau and Chan, 2003; Shiohara et al., 2005; Fujii et al., 2007). Similarly to the studies inside subway carriages or subway stations, toluene (T) was also found to be the most abundant VOCs both indoor and outdoor of the selected subway stations in Shanghai (Table 1). The highest toluene concentration ($117.4\text{ }\mu\text{g}/\text{m}^3$) occurred in the mezzanine of ZSP Station. The highest benzene (B) concentration ($27.0\text{ }\mu\text{g}/\text{m}^3$) was detected in the platform of SRS. Benzene, toluene, ethylbenzene (E) and xylenes (X) (collectively as BTEX) at the platforms and mezzanines inside the stations averaged (10.3 ± 2.1), (38.7 ± 9.0), (19.4 ± 10.1) and (30.0 ± 11.1) $\mu\text{g}/\text{m}^3$, respectively. As shown in Table 2, benzene levels inside the subway stations of Shanghai were comparable to that found in Metro carriages

Table 1 Mean levels in platforms, mezzanines and outdoor (unit: $\mu\text{g}/\text{m}^3$)

Compound	Carcinogenicity ^a	Unit risk ($\mu\text{g}/\text{m}^3$)	Platform			Mezzanine			Outdoor			I/O ratio ^e		
			Mean \pm 95% C.I.	Medium	Range	Mean \pm 95% C.I.	Medium	Range	Mean \pm 95% C.I.	Medium	Range	Mean \pm 95% C.I.	Medium	Range
Benzene	1	2.9E-5 ^b /6E-6 ^d	11.8 \pm 3.7	11.1	4.2–27.0	8.9 \pm 2.2	8.2	3.1–19.7	6.8 \pm 1.1	6.4	4.2–11.2	1.4 \pm 0.3	1.3	0.6–2.4
Toluene	3		37.2 \pm 12.0	28.4	17.3–94.0	40.2 \pm 13.6	36.2	13.7–117.4	32.2 \pm 13.5	21.8	11.2–106.9	1.4 \pm 0.4	1.2	0.6–3.2
Ethylbenzene	2B	5.0E-7 ^c	17.9 \pm 12.8	9.7	3.9–98.1	20.7 \pm 15.8	9.3	5.1–126.7	8.1 \pm 3.0	6.3	2.9–23.7	2.1 \pm 1.1	1.5	1.0–9.4
<i>m/p</i> -Xylene	3		22.6 \pm 11.8	10.8	6.9–71.8	21.5 \pm 12.3	10.9	5.4–93.7	10.1 \pm 3.7	8.5	2.8–31.3	1.9 \pm 0.7	1.5	0.9–6.4
<i>o</i> -Xylene	3		8.1 \pm 3.9	4.2	2.7–24.0	7.8 \pm 3.9	4.0	2.3–30.8	3.9 \pm 1.3	3.5	1.4–11.5	1.9 \pm 0.6	1.6	0.9–5.8
1,3,5-TMB ^f			2.5 \pm 1.7	1.1	0.4–11.4	1.5 \pm 0.8	0.7	0.3–6.2	2.5 \pm 1.7	0.8	0.3–11.4	2.3 \pm 1.6	1.7	0.0–11.3
1,2,4-TMB			11.7 \pm 8.9	4.9	1.2–62.0	6.4 \pm 3.4	2.3	1.0–23.0	11.6 \pm 9.0	2.0	1.2–62.0	3.2 \pm 2.0	2.4	0.0–13.8
CT	2B	4.2E-5 ^b	1.2 \pm 0.4	0.9	0.4–3.0	1.2 \pm 0.4	1.1	0.5–3.0	0.9 \pm 0.3	0.8	0.4–2.4	1.4 \pm 0.4	1.2	0.5–3.5
VC	1	1E-6 ^d	2.0 \pm 1.6	0.6	0.0–11.5	2.4 \pm 1.7	1.6	0.0–12.9	1.8 \pm 1.3	0.9	0.0–9.0	3.2 \pm 3.0	1.5	0.1–21.7
1,2-DCP			1.2 \pm 1.5	0.5	0.1–11.1	0.9 \pm 0.6	0.5	0.1–4.7	0.4 \pm 0.1	0.3	0.1–1.2	1.3 \pm 0.3	1.6	0.5–2.3
TCPE	2A	2.0E-6 ^b /4.3E-7 ^d	2.9 \pm 1.1	2.5	0.8–9.0	4.4 \pm 2.2	2.5	0.5–14.4	1.4 \pm 0.9	0.7	0.3–6.3	4.0 \pm 1.4	3.6	1.2–11.8
TeCE	2A	5.9E-6 ^b /4.3E-7 ^d	1.3 \pm 0.7	0.8	0.2–5.2	1.3 \pm 0.7	1.2	0.2–6.0	0.8 \pm 0.3	0.6	0.2–1.8	1.9 \pm 1.4	1.3	0.4–11.1
CB			0.3 \pm 0.1	0.2	0.0–0.6	0.3 \pm 0.1	0.3	0.1–0.5	0.2 \pm 0.1	0.2	0.0–0.6	1.7 \pm 0.6	1.5	0.5–5.0
<i>m</i> -DCB			0.2 \pm 0.3	0.1	0.0–1.9	0.2 \pm 0.1	0.1	0.0–0.8	0.1 \pm 0.1	0.0	0.0–0.5	9.5 \pm 8.9	2.9	0.2–57.6
<i>o</i> -DCB			0.0 \pm 0.0	0.0	0.0–0.1	0.0 \pm 0.0	0.0	0.0–0.2	0.0 \pm 0.0	0.0	0.0–0.1	1.5 \pm 0.6	1	0.6–4.6
<i>p</i> -DCB	2B	1.1E-5 ^b	3.9 \pm 1.6	3.2	0.3–9.8	4.3 \pm 1.5	3.4	1.0–9.8	3.3 \pm 1.4	2.2	0.5–9.1	1.9 \pm 0.8	1.3	0.5–5.1

^a IARC, 2004; ^b hot spots unit risk by California Environmental Protection Agency, Office of Environmental Health Hazards Assessment (Cal EPA, 2002); ^c Cumulative Exposure Project of US EPA (Caldwell et al., 1998); ^d WHO, 2006; ^e for calculating average indoor to outdoor (I/O) ratios, samples both in platforms and in mezzanines at a station were put together to compute mean indoor levels; ^f TMB: trimethylbenzene.

Table 2 Comparison of the mean BTEX levels with those reported in other subway systems

City	Sampling time	Locations in subway systems	Concentration ($\mu\text{g}/\text{m}^3$)				Reference
			B	T	E	X	
Guangzhou, China	May 2001	Subway carriages	7.6	38	5.6	9.3	Chan et al., 2003
Hong Kong, China	Nov 2001 to Mar 2002	Subway carriages	3.6	78.8	6.6	10.6	Lau and Chan, 2003
Mexico City, Mexico	Jun 2002	Subway carriages	11.4	62.8	11.3	33.3	Shiohara et al., 2005
Sao Paulo, Brazil	Jun 2005	Subway carriages					Fujii et al., 2007
		CLI platform	5.7	22.7	4.7	11.9	
		CLI mezzanine	5.6	22.2	5.6	13.1	
		CLI outdoor	5.7	22.8	4.7	12.2	
		PSE line1 platform	4.1	16.8	2.7	7.2	
		PSE mezzanine	4.4	17.8	2.6	6.7	
		PSE outdoor	4.3	21.3	2.9	7.6	
		PSE line3 platform	3.8	18	2.7	6.9	
Berlin, Germany	Summer and winter, 1995	Subway carriages	5.4	33	5.5	20.4	Fromme et al., 1997
Berlin, Germany	Summer and winter, 1996	Subway carriages	7.4	31	5.4	16.7	Fromme et al., 1997
Boston, USA	Nov 1989 to Jan 1990	Subway carriages	6.9	30.8	2.5	13.4	Chan et al., 1991
Shanghai, China	Jul 2007	Platform	11.8	37.2	17.9	30.7	This study
		Mezzanine	8.9	40.2	20.7	29.3	
		Outdoor	6.8	32.2	8.1	14	

B: benzene; T: toluene; E: ethylbenzene; X: xylenes

in Mexico City (Shiohara et al., 2005), but higher than those reported inside carriages or at stations in subway systems of other cities like Boston (Chan et al., 1991), Berlin (Fromme et al., 1997), Guangzhou (Chan et al., 2003), Hong Kong (Lau and Chan, 2003) and Sao Paulo (Fujii et al., 2007). Toluene levels inside the subway stations were quite similar to those previously reported inside subway carriages of Guangzhou (Chan et al., 2003), Berlin (Fromme et al., 1997) and Boston (Chan et al., 1991). They were relatively lower compared to those reported in the subway carriages of Mexico City (Shiohara et al., 2005) or Hong Kong (Lau and Chan, 2003), but much higher than those reported inside subway carriages or stations in Sao Paulo (Fujii et al., 2007). Ethylbenzene and xylenes were the highest when compared to those inside subway carriages or stations in other cities. The average outdoor levels of benzene and toluene were 6.8 and 32.2 $\mu\text{g}/\text{m}^3$, higher than their average ambient levels in winter 2001 in Shanghai, which were 4.2 $\mu\text{g}/\text{m}^3$ (1.2 ppbV) and 20.9 $\mu\text{g}/\text{m}^3$ (5.1 ppbV), respectively (Barletta et al., 2005).

Although mean benzene levels at platforms in this study were two times of that in subway stations of Sao Paulo (Fujii et al., 2007), they were well below the 110 $\mu\text{g}/\text{m}^3$ guideline levels set for indoor environment in China according to the indoor air quality standard (GB/T 18883-2002). As a carcinogenic compound of wide concern, benzene has no identifiable threshold below which there is no risk to human health. According to WHO (2006), the excess lifetime risk of leukaemia for benzene at an air concentration of 1 $\mu\text{g}/\text{m}^3$ is 6×10^{-6} . That is, the concentrations of airborne benzene associated with an excess lifetime risk of 1/10,000, 1/100,000 and 1/1,000,000 are 17, 1.7 and 0.17 $\mu\text{g}/\text{m}^3$, respectively. European Commission (EC) Directive 2000/69/EC set a limit of 5 $\mu\text{g}/\text{m}^3$ (annual mean) for benzene in ambient air for the protection of human health. This limit was also adopted by Committee on the Medical Effects of Air Pollutants as an indoor air guideline in United Kingdom. For short-term guideline levels, Hong Kong Environmental Protection Department set a

guideline level of 16.1 $\mu\text{g}/\text{m}^3$ (8-hr mean) for benzene in indoor environment. The guideline level of 110 $\mu\text{g}/\text{m}^3$ (1-hr mean) for indoor benzene in mainland China seems to be unreasonably much higher when compared to available guideline levels adopted by other countries/organizations for benzene either in ambient air or in indoor environment. Although the benzene exposure levels in this work were well below the indoor guideline levels of mainland China, they were still quite higher and may pose health risks especially to those who spend a longer time working inside the subway systems. Nevertheless, as illustrated later benzene was mainly transported from outdoor instead of from indoor emission sources.

2.2 Chlorinated hydrocarbons

Chlorinated hydrocarbons (CHs) are present in indoor environment due to indoor/outdoor air exchange or from indoor applications of products containing chlorinated solvents. For example, tetrachloroethylene, a most popular dry-cleaning agent, typically had higher levels in drying-cleaning facilities (Chiappini et al., 2009), buildings where dry cleaners using TeCE were operated (McDermott et al., 2005), or residential buildings near drying-cleaning facilities (Kwon et al., 2006). CHs like TrCE and pDCB can be released to indoor air due to the use of consumer products (Shiohara et al., 2008), or vapor intrusion from groundwater through underground walls and floors (Hers et al., 2001). The occurrence of CHs in many consumer products, as well as their multiple pathways to enter indoor air, makes them an important class of air toxics detected in various indoor environments (Pellizzari et al., 1986; Hartwell et al., 1992; Kostianen, 1995; Lee et al., 2002; Sexton et al., 2004; Sakai et al., 2004; Tang et al., 2005). However, no reports are available about CHs inside subway carriages or in subway stations.

In the present study, carbon tetrachloride (CT), vinyl chloride (VC), chloroethane, 1,2-dichloropropane (DCP), TrCE, TeCE, chlorobenzene (CB) and dichlorobenzenes were widely detected in the subway stations. TrCE, TeCE,

pDCB, VC and CT are the most abundant chlorinated hydrocarbons inside the stations (platforms and mezzanines) with average levels of (3.6 ± 1.3) , (1.3 ± 0.5) , (4.1 ± 1.1) , (2.2 ± 1.1) and $(1.2 \pm 0.3) \mu\text{g}/\text{m}^3$, respectively. The highest concentrations of VC, TeCE and pDCB all occurred at the mezzanine of ZSP Station, which reached 12.9, 6.1 and $9.8 \mu\text{g}/\text{m}^3$, respectively. The highest concentration of TrCE, $14.4 \mu\text{g}/\text{m}^3$, was detected in the mezzanine of XJH Station. A comparison of their levels at the platforms and mezzanines with those previously reported in various indoor environments is presented in Table 3. The average concentrations of TrCE in the platforms and mezzanines were higher than those reported in homes (Pellizzari et al., 1986; Kostianen, 1995; Lee et al., 2002; Kinney et al., 2002; Sexton et al., 2004; Zhu et al., 2005), stores and restaurants (Loh et al., 2006) and trains and buses (Guo et al., 2004), but was much lower when compared to levels reported in a home in Los Angeles (Hartwell et al., 1992), a home in Nagoya, Japan (Sakai et al., 2004) or a shopping mall in Guangzhou (Tang et al., 2005). TeCE inside the subway stations of Shanghai were agreeable to those reported indoor levels except that observed in a home in Los Angeles (Hartwell et al., 1992), a home in Harlem, New York (Kinney et al., 2002) and a shopping mall in Guangzhou. pDCB is widely used in moth repellents and deodorizing products. The levels of pDCB in the platforms and mezzanines were also comparable to previously reported indoor levels (Table 3) except that reported in homes of Nagoya, Japan (Sakai et al., 2004) and Harlem, New York City (Kinney et al., 2002). A survey of VOCs in a wide range of urban microenvironments in Birmingham, UK revealed much higher levels of pDCB in department stores and libraries with means of 23.4 and $12.8 \mu\text{g}/\text{m}^3$, respectively (Kim et al., 2001). pDCB occurred inside the stations might be related to their use in toilets as deodorizing products. Since the outdoor samples were collected near the station entrances located at urban roadsides, the outdoor levels of TrCE, TeCE and CT in the present study averaged 1.4, 0.8 and $0.9 \mu\text{g}/\text{m}^3$, and were reasonably higher than the

ambient averages in Shanghai during January–February 2001, which were $0.1 \mu\text{g}/\text{m}^3$ (36 pptV), $0.4 \mu\text{g}/\text{m}^3$ (54 pptV) and $0.7 \mu\text{g}/\text{m}^3$ (107 pptV), respectively (Barletta et al., 2006).

2.3 Concentration variation among different stations

Aromatic and chlorinated hydrocarbons inside the stations revealed no significant difference ($p > 0.05$) when comparing their means between morning, afternoon and evening rush-hours. However, as shown in Fig. 2, they varied substantially in the five stations. The outdoor levels, different geophysical locations and traffic densities, as well as different dispersion conditions, might all have great impacts on the indoor levels. ZSP, SRS and XJH sites are transfer stations in densely populated old urban areas, while CP and LJZ are stations in the relatively new sub-urban areas with much less pollution sources and traffic. ZSP and SRS in the business districts with heavy traffic showed higher outdoor BTEX levels; they also had significantly higher outdoor benzene levels ($p < 0.05$) than CP or LJZ.

At mezzanines, there were significantly higher ($p < 0.05$) toluene levels at SRS and XJH when compared to that at LJZ, and for TrCE ($p < 0.05$) at ZSP and XJH to that at CP or LJZ; on the platforms, higher toluene levels were found in XJH than those in LJZ, and TrCE and pDCB in SRS were significantly higher ($p < 0.01$) than those in CP or LJZ. These variations among levels inside the stations were not only related to their different fresh air supplies from outdoor, but also related to their differences in indoor emissions such as from fast-food courts and restaurants (Tsai et al., 2003; Tang et al., 2005) located in stations, and from floors and furniture coatings in large shopping malls (Yu and Crump, 1998) connected to the subway by aisles.

Average indoor (platform and mezzanine) to outdoor (I/O) ratios of the aromatic and chlorinated hydrocarbons are listed in Table 1. It could be found that I/O ratios for all species were bigger than 1.0, suggesting overall higher exposure levels inside the stations than outdoor.

Table 3 Comparison of mean levels of selected chlorinated hydrocarbons in different microenvironments

Location	TrCE ($\mu\text{g}/\text{m}^3$)	TeCE ($\mu\text{g}/\text{m}^3$)	pDCB ($\mu\text{g}/\text{m}^3$)	Reference
Home, Baton Rouge/Geismar, USA	0.08	0.4	2.1	Pellizzari et al., 1986
Home, Los Angeles, USA	8.9	1.2	2.8 ^a	Hartwell et al., 1992
Home, Los Angeles, USA	NA	4.38	1.59 ^a	Hartwell et al., 1992
Home, Finland	0.97	0.46	0.65	Kostianen, 1995
Home, Harlem, New York, USA	1.26	7.53	54.9	Kinney et al., 2002
Home, Hong Kong, China	1.8	2.5	2.6	Lee et al., 2002
Home, USA	0.5	2.9	1.2	Sexton et al., 2004
Home, Nagoya, Japan	4.96	3.72	40	Sakai et al., 2004
Home, Uppsala, Sweden	0.16	0.1	1.03	Sakai et al., 2004
home, Ottawa, Canada	0.06	1.15	NA	Zhu et al., 2005
Shopping mall, Guangzhou, China	11.4	7.4	12.3	Tang et al., 2005
Stores (GM), Boston, USA	0.43	1.41	2.4	Loh et al., 2006
Dinings, Boston, USA	0.23	2.09	1.45	Loh et al., 2006
Mass Transit Railway, Hong Kong, China	0.38	0.45	NA	Guo et al., 2004
Buses, Hong Kong, China	0.76	0.65	NA	Guo et al., 2004
Subway platforms, Shanghai, China	2.9	1.3	3.9	This study
Subway mezzanines, Shanghai, China	4.4	1.3	4.3	This study

NA: not available; ^a *m,p*-dichlorobenzene.

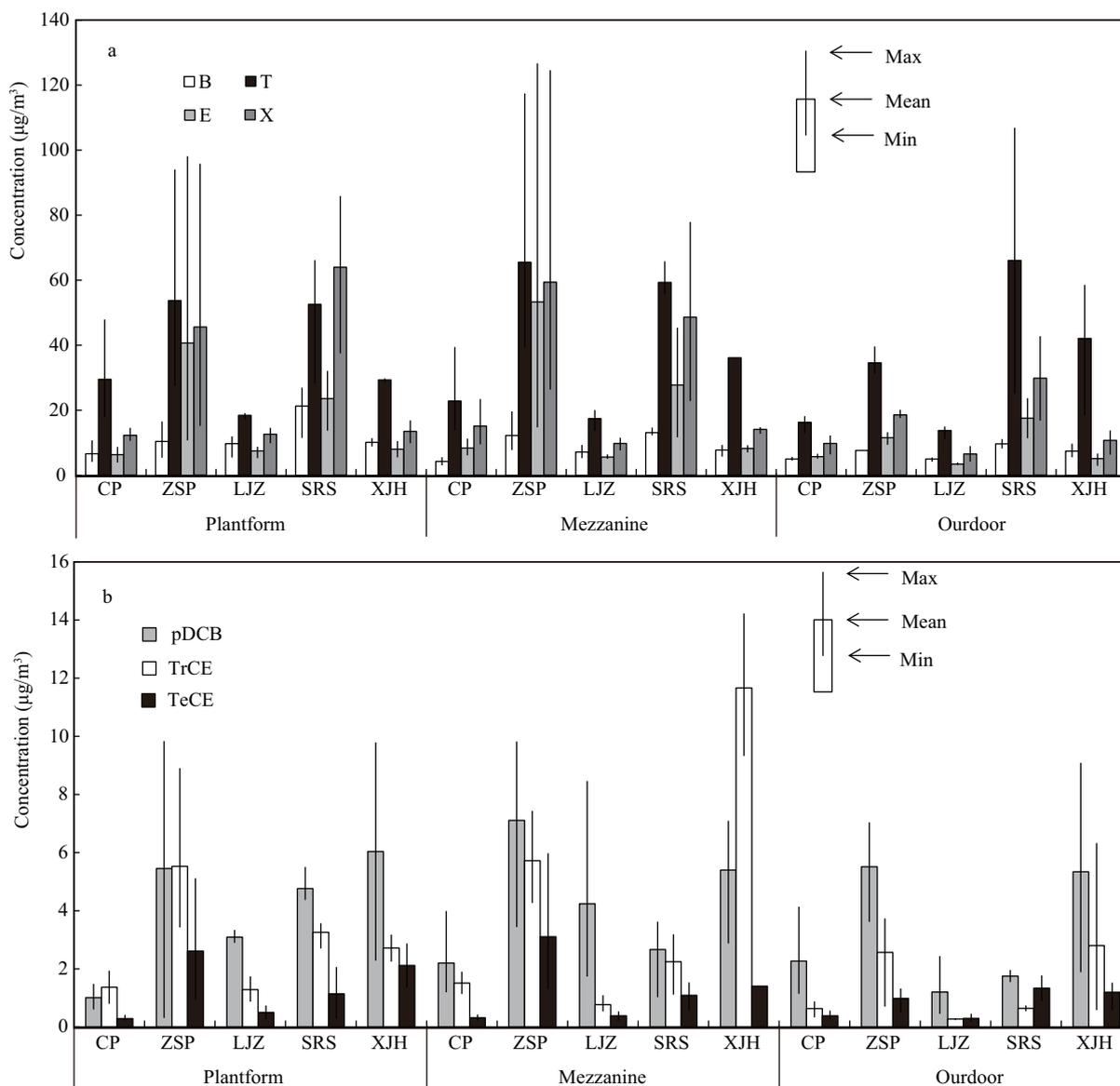


Fig. 2 Means and ranges of BTEX (a) and chlorinated solvents (b) in platforms, mezzanines and outdoor of the five stations.

However, the ranges of I/O ratios showed that their indoor levels were not uniformly higher than their outdoor ones. In fact, only benzene and TrCE had significantly higher indoor (platforms and mezzanines) levels than outdoor ($p < 0.05$). Moreover, only benzene at platforms and TrCE in mezzanines showed significantly higher levels ($p < 0.05$) than that outdoor. The levels of chlorinated and aromatic hydrocarbons at platforms were not significantly different from those at mezzanines. Although I/O ratio is used to indicate source contribution, it may be not effective to reflect indoor/outdoor relationship due to ventilation status and sampling design (Tang et al., 2005). In the present study, the stations are centrally air-conditioned. Indoor/outdoor air exchanges were not only achieved via introducing fresh air by the mechanical ventilation systems, but also through the gates in the mezzanines open to streets or department stores. VOCs measured inside and outside the subway stations in the present study were not exactly paired ones, so the calculated I/O ratios were not relevant and improper to be used to infer indoor sources or the infiltration of

pollutants from outdoors.

2.4 Source implications

Since I/O ratios are not enough to infer source contribution, here we attempt to explore the possible sources of the VOCs using correlation analysis, especially their correlation with some specific markers, like methyl *tert*-butyl ether (MTBE). Chang et al. (2003) illustrated the role of MTBE as an exclusive indicator of traffic-related emissions. Hsieh et al. (2006) confirmed that MTBE is more suitable than other VOCs as a reference compound indicating traffic emissions because of its sole consumption in gasoline formulation. Table 4 summarizes coefficients among BTEX and MTBE in platforms, mezzanines and outdoors. As shown in Table 4, highly mutual significant correlations ($p < 0.001$) were observed among outdoor BTEX. These good mutual correlations might indicate that BTEX came predominantly from a single source (Wang et al., 2002; Chan et al., 2003), probably traffic-related emission due to their significant correlation ($p < 0.05$).

with MTBE. The average B/T ratio in outdoor (1/4.7) was almost the same as previously reported (1.2/5.1) in Shanghai (Barletta et al., 2005). Highly significant mutual correlations were also found for BTEX at the platform ($p < 0.001$) and mezzanine ($p < 0.01$). In addition, BTEX measured both at the platforms and the mezzanines showed significant correlations with those measured outdoor. The good correlations of BTEX among platforms, mezzanines and outdoor might suggest that these aromatic hydrocarbons largely shared same type of sources, and the significant correlations between MTBE and BTEX species in platform ($R > 0.89$, $p < 0.001$), mezzanine ($R > 0.68$, $p < 0.05$) and outdoor ($R > 0.68$, $p < 0.05$) implied that traffic-related emission was the dominant source of BTEX which mainly came from outdoor through indoor/outdoor air exchange.

No significant correlations were found between TrCE/pDCB and aromatic species, or between TrCE/pDCB and MTBE at the platforms and mezzanines (Table 4), suggesting that TrCE or pDCB in subway stations had different sources and emission patterns compared to BTEX, and indoor emission would be major source of TrCE and pDCB. Interestingly, TeCE showed significant correlation with MTBE outdoor or at mezzanines, with BTEX outdoor and with toluene at mezzanines, but poor correlations were found at platforms with BTEX or MTBE. As a solvent mainly used for drying clean in urban area, outdoor TeCE were expected to be positively correlated with population density in the neighborhood; while MTBE were supposed to be positively correlated with traffic density. Therefore, significant correlation between TeCE and MTBE does not suggest that TeCE were related to traffic emission; it was probably resulted from the bigger usage of TeCE in the districts near the stations with higher population and traffic density. Similarly, the good correlation between TeCE and TrCE or between TrCE and pDCB in the outdoor ambient air (Table 4) does not imply that they shared the same sources, but their emission strengths in the neighborhood of different stations might change in the same pattern.

At mezzanines, TeCE were significant correlated with both MTBE and toluene, but not with other aromatic hydrocarbons. The good correlation for TeCE with MTBE implied that TeCE possibly had contribution of outdoor air intrusion, however the poor correlation with B/E/X suggested that outdoor air is not the only dominant source as BEX. The good correlation with toluene indicated that TeCE might have indoor and outdoor source emissions from small shops inside station, as well as aisles connected to large department stores with indoor materials or consumer products, in which toluene is a widely used solvent in paints, paint thinners, fingernail polish, lacquers, adhesives, rubber and in some printing and leather tanning processes (ATSDR, 2009).

The contribution of solvent emission can be also indicated by the B/T ratio. The outdoor and the mezzanine samples had averaged B/T ratios of 0.21 and 0.22, respectively. These ratios were almost the same but quite lower compared to ca. 0.5 in vehicle exhaust (Wang et

al., 2002; Barletta et al., 2005) or those detected in the platform samples (0.32) in the present study. At platforms TrCE had no significant correlation with MTBE or any aromatic hydrocarbons, indicating indoor emission could be its major source.

3 Conclusions

A survey of organic HAPs in selected subway stations of Shanghai, China, was presented in this work. Although major toxic aromatic and chlorinated hydrocarbons showed higher levels inside the stations than outdoor, but no significant differences were found except for benzene and TrCE. Specifically, only benzene on platforms and TrCE in mezzanines showed significantly higher average levels ($p < 0.05$) than outdoor. Benzene levels inside the stations were all well below the guideline level of $110 \mu\text{g}/\text{m}^3$ set for indoor environment in China, but extremely higher than the levels set by other countries. BTEX inside the stations were predominantly transported from outdoor due to air exchange and minor contribution was from indoor emissions except that toluene might also have indoor sources at mezzanines. The good correlation between BTEX and MTBE also indicated that BTEX were from vehicle-related emissions. The correlation analysis presented that TrCE and pDCB detected inside the stations came mainly from indoor sources instead of intrusion of outdoor air. TeCE was mainly from indoor sources at the platforms and outdoor air intrusion at the mezzanines.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 40821003), the Guangdong Natural Science Foundation (No. 7118013), the State Key Laboratory of Organic Geochemistry and the Hong Kong Polytechnic University Joint Student Program. The efforts of anonymous reviewers during review have greatly improved the quality of this manuscript and are sincerely appreciated.

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