Journal of Hazardous Materials 183 (2010) 574–582

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Characteristics and personal exposures of carbonyl compounds in the subway stations and in-subway trains of Shanghai, China

Yanli Feng*, Cuicui Mu, Jinqing Zhai, Jian Li, Ting Zou

Institute of Environmental Pollution and Health, School of Environmental and Chemical Engineering, Shanghai University, Shanghai 200444, China

ARTICLE INFO

Article history:
Received 11 May 2010
Received in revised form 9 July 2010
Accepted 12 July 2010
Available online 21 July 2010

Keywords:
Carbonyl compounds
Subway station
In-subway train
Concentration
Ozone
Exposure

ABSTRACT

Carbonyl compounds including their concentrations, potential sources, diurnal variations and personal exposure were investigated in six subway stations and in-subway trains in Shanghai in June 2008. The carbonyls were collected onto solid sorbent (Tenax TA) coated with pentafluorophenyl hydrazine (PFPH), followed by solvent extraction and gas chromatography (GC)/mass spectrometry (MS) analysis of the PFPH derivatives. The total carbonyl concentrations of in-subway train were about 1.4–2.5 times lower than in-subway stations. A significant correlation ($R > 0.5$, $p < 0.01$) between the concentrations of the low molecular-weight carbonyl compounds ($<C_5$) and ozone was found in the subway stations. The diurnal variations in both the subway station and in-subway train showed that the concentrations of most carbonyls were much higher in the morning rush hour than in other sampling periods. Additionally, pronounced diurnal variations of acetaldehyde concentration before and after the evening peak hour in the subway train suggested that passengers contributed to high acetaldehyde levels. The personal exposure showed that the underground subway stations were important microenvironment for exposure to formaldehyde and acetaldehyde.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Shanghai is situated at the east coast of China (Longitude 120°51′–122°12′ E, latitude 30°40′–31°53′ N, Fig. 1(a)) and is considered to be one of the most prosperous and densely populated cities in the world. Subway is a speedy, safe, comfortable and convenient means of transportation for traveling around Shanghai. Daily ridership including young students, workers and senior citizens averaged 3.065 million in 2008 and set a record of 4.735 million on September 30, 2009. Consequently, the air quality is very important to the public health. Previous studies have been reported on field investigation of personal exposure assessment of air pollution in the subway stations, such as aerosol particles [1], PM_{10} and $PM_{2.5}$ [2–5], VOCs [6], manganese [7], benzene [2], airborne fungi [8], etc. However, the personal exposure to the carbonyls in-subway station is seldom reported in existing literature, even though they have adverse health effects both for passengers and subway workers.

Carbonyl compounds (aldehydes and ketones) in the air continue to receive scientific and regulatory attention as their important role in photochemistry and for the toxic air contaminants which are suspected carcinogens and can cause, eye irritants, and mutagens to human [9–13]. Recently, numerous studies were focused on quantifying and assessing personal exposure to carbonyls in the microenvironments such as ballrooms [12], residential houses [14], museum [15], office rooms [16], temple [17], and hospital [18], etc. Whereas, exposure to carbonyls in-subway and subway station probably is more important because more and more people take the subway with urban expansion. In addition, it is estimated that people living in urban areas in the developed countries spend approximately 8% of their daily commuting time on subway [19,20]. Newly released "2010 Chinese New-Approach Urbanization report" shows that commuters in China now top the world in commuting time (from home to work). According to this report, the average commuting time is over 30 min in 17 out of the 50 cities that have been investigated, with Beijing (52 min) topping the list, followed by Guangzhou with an average of 48 min, Shanghai with 47 min and Shenzhen with 46 min. Therefore, there is an urgent need for field research to measure carbonyls in Shanghai subway in order to establish a management plan against exposure to carbonyls. But unfortunately, there is few study that focused on the air pollution of carbonyls in-subway, particularly in Shanghai.

The commonest method for the determination of gaseous carbonyls was to collect carbonyls onto 2,4-dinitrophenylhydrazine (DNPH) coated solid sorbent followed by solvent extraction and analysis of the derivatives by high-pressure liquid chromatography [21,22]. In this study, pentafluorophenyl hydrazine (PFPH) coated solid sorbent as the derivative agent followed by gas chromatographic (GC)/mass spectrometric (MS) detection was employed for the better resolution and sensitivity and lower limit of detection (LOD) [23,24]. Both indoor and outdoor measurements of carbonyls

* Corresponding author. Tel.: +86 21 66137731; fax: +86 21 66137731.
E-mail address: fengyanli@shu.edu.cn (Y. Feng).

0304-3894/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2010.07.062

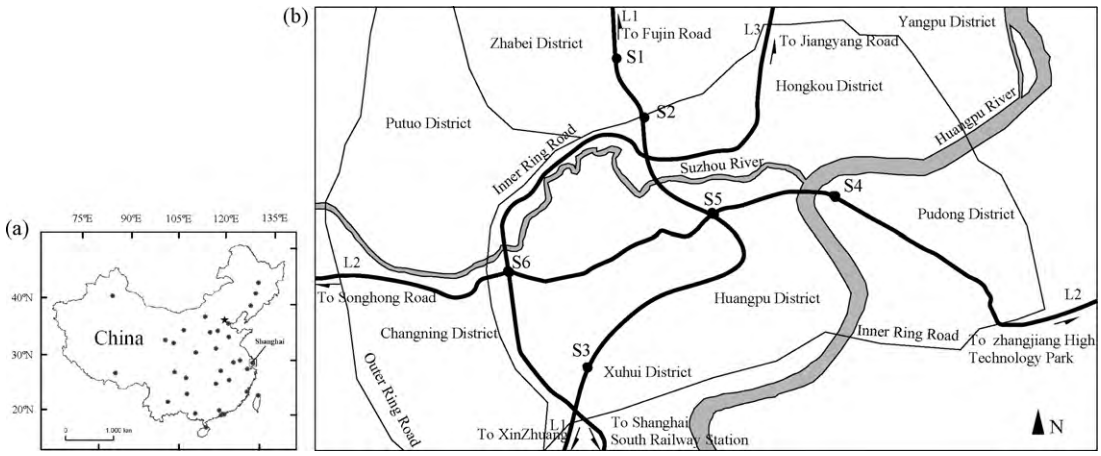

Fig. 1. The sketch map of sampling sites.

were carried out in Shanghai metro system including six subway stations and in-subway trains of three main-subway lines on actual commuting routes. The overall aim of this paper is to characterize the levels of carbonyls pollution in-subway stations and in-subway trains and then to provide fundamental research data which can be used to reduce the health risks both for the passengers and subway workers.

2. Experimental

2.1. Sampling sites

At present, Shanghai has ten subway lines in operation, totally approximate 330 km. The system incorporates both subway and light railway lines. Six subway stations and subway trains of three subway lines were investigated in this study (Fig. 1). Samples were collected on 2–22 June 2008. The subway stations selected were classified as three types including the large scale, the medium scale and the small scale according to the passenger throughput of three grades: less than 50,000, between 50,000 and 100,000, and more than 100,000 per day on weekdays, respectively. The detailed information related to these stations and the subway lines was shown in Table 1 and Fig. 1. For the selected subway station, indoor measurements were carried out at the middle of platforms and 1.5 m above ground level. For in-subway train samples, we traveled as passengers holding the sampler. In general, most lines were within the urban area, namely within the Outer Ring Road of Shanghai. The measured subway trains were randomly chosen without any

Table 1
Information about the selected subway stations and lines.

Sampling site (ID)		Used year	Sampling days/number	Characteristics of subway stations and lines
Small scale stations	Shanghai Circus World (S1)	4 years	2/12 (10 for indoor and 2 for outdoor)	An underground station with 3 exits, central air condition and platform screen door of Line 1 in Zhabei District
	North Zhongshan Road (S2)	4 years	1/7 (5 for indoor and 2 for outdoor)	An underground station with 3 exits, central air condition and platform screen door of Line 1 in Zhabei District
Medium scale stations	Xujiahui (S3)	13 years	2/12 (10 for indoor and 2 for outdoor)	An underground station with 12 exits, central air condition and platform screen door of Line 1 in Xuhui District
	Lujiazui (S4)	8 years	1/7 (5 for indoor and 2 for outdoor)	An underground station with 5 exits and central air condition of Line 2 in Pudong District
Large scale stations	People Square (S5)	15 years	2/12 (10 for indoor and 2 for outdoor)	A transfer underground station for lines 1, 2 and 8, with 15 exits, central air condition and platform screen door in Huangpu District
	Zhongshan Park (S6)	8 years	2/12 (10 for indoor and 2 for outdoor)	A transfer underground station for lines 2, 3 and 4, with 8 exits and central air condition in Changning District
Line 1	Fujin Road, XinZhuang (L1)	–	2/10 (all for indoor)	A 40-km track with 13 ground stations and 15 underground stations. The average journey time is about 70 min (semi-subway line)
Line 2	Songhong Road, Zhangjiang High Technology Park (L2)	–	2/10 (all for indoor)	A 25.2-km underground track with a whole of 17 underground stations. The average journey time is about 70 min (subway line)
Line 3	North Jiangyang Road, Shanghai South Railway Station (L3)	–	2/10 (all for indoor)	A 40.3-km track with a whole of 29 ground stations. The average journey time is about 70 min (light rail)

selection criteria. Smoking in public transportation was strictly prohibited in subway stations and subway trains, samples were collected within the service time between 6:30 a.m. and 10:30 p.m. on one or two consecutive days for each station or line. An outdoor site at the station exit was also investigated at the same time of each measurement (Two 3-h samples were collected on the morning and evening peak hours for each selected station).

2.2. Reagents

Hexane was purchased from Merck Corporation, Germany (GC Grade). Aldehydes and ketones from C_1 to C_{10}, including formaldehyde, acetaldehyde, propionaldehyde, acetone, acrolein, crotonaldehyde, n-butyraldehyde, valeraldehyde, isovaleraldehyde, cyclohexanone, hexaldehyde, benzaldehyde, heptaldehyde, o-tolualdehyde, m-tolualdehyde, p-tolualdehyde, octylaldehyde, 2,5-dimethylbenzaldehyde, nonanaldehyde, decylaldehyde, and 4-fluorobenzaldehyde (acting as an internal standard) were purchased from ChemService Corporation (West Chester, PA, USA). Pentafluorophenylhydrazine (PFPH), employed as a derivative agent, was from Sigma–Aldrich, USA, and used without further purification. Tenax TA (60/80 mesh) was from Supelco Corporation, USA.

2.3. Sampling and analysis

Carbonyls were collected by drawing air through the two-section design sampling tube (6 mm o.d., 4 mm i.d. and 8 cm long) with a personal sampling pump (SKC, USA) at a flow rate of ~80 mL/min. The exact flow rate was recorded by a digital flow meter (DryCal DC Lite, Bios Corp., USA) before and after each sample collection. The ozone concentration was also recorded every 20 min during sampling using a portable aeroqual ozone meter series 300 (Auckland, New Zealand). The sampling period at the platform and in-subway train was 3 and 2 h, respectively. Pre-experiment was conducted before sampling and no breakthrough was found for all carbonyls in such sampling periods. The PFPH coated Tenax TA is packed into two separate sections (100 mg for the front section and 30 mg for the back section) in a glass tube with a coating amount of 971 nmol PFPH per 100 mg Tenax TA. The two-section design allows convenient checking of collection efficiency and breakthrough. After collection, the two parts of Tenax TA were removed and extracted separately. The extracting and processing of the samples were described in detail in our previous study [24].

Separation of the carbonyl compounds was performed on a GC (Agilent 6890N, USA) equipped with an HP-5MS column (5% phenyl Methyl Siloxane, 30 m × 250 μm × 0.25 μm film thickness). The column temperature was maintained at 72 °C for 1 min after injection, then programmed to 110 °C at a rate of 8 °C min^{-1}, and then to 175 °C at 4.5 °C min^{-1}, kept at 175 °C for 2 min, and finally heated to 200 °C at a rate of 2.5 °C min^{-1}. The MSD was operated in electron ionization (EI) mode at 70 eV and the GC/MS interface temperature was 290 °C. The mass spectrometer was initially operated in scan mode with a mass range of 50–400 to identify the most abundant ions and the molecular ion of each compound. These characteristic ions were then used to identify and quantify the carbonyl compounds present in field samples in selective ion monitoring (SIM) mode.

2.4. Quality assurance and quality control

The solvents were GC grade and tested for purities when a new lot was used. Three random blank sampling tubes were analyzed for each lot to check the lab blank, while at least one field blank sample was collected for each set of samples and no target carbonyls were found in the blank samples. Two field samples in one sampling site were chosen randomly to evaluate breakthrough by analyzing the front and the back part separately, and more than 95% of the target carbonyls were collected in the front part of the sampling tube. The calibration curves were prepared by using five standard concentrations (from 0.1 to 10 μg mL^{-1}) covering the concentration of interest for each work and the correlation coefficients (R^2) were ranging from 0.995 to 1.0 for 20 carbonyl compounds. The solvent extraction efficiencies were in the range of 95.8 ± 1.0% to 99.6 ± 0.8%. Relative standard deviations (RSDs) for replicate analyses were less than 4.6%. RSDs of collocated samples were below 13.2%. Recoveries were determined by analyzing blank sampling tubes spiked with known amounts of the standard solution of PFPH-carbonyl derivatives (10uL, 1 μg mL^{-1}). The recoveries were from 93 ± 5% for p-tolualdehyde to 109 ± 6% and for formaldehyde. Method detection limits (MDLs) were determined by analyzing seven blank PFPH sampling tubes. The front and the back part of each blank sampling tube were analyzed separately, and then the results of the two portions were added together. The MDLs were in the range of 3.7–11.6 ng per tube for various carbonyls.

3. Results and discussion

3.1. Indoor carbonyl levels and their possible sources

Nineteen carbonyl compounds were measured in the subway stations and subway trains samples, including formaldehyde, acetaldehyde, propionaldehyde, acetone, acrolein, crotonaldehyde, n-butyraldehyde, valeraldehyde, isovaleraldehyde, cyclohexanone, hexaldehyde, benzaldehyde, heptaldehyde, o-tolualdehyde, m-tolualdehyde, p-tolualdehyde, octylaldehyde, nonanaldehyde, and decylaldehyde. Arithmetic mean concentrations and standard deviations (SD) of these carbonyl compounds are listed in Table 2. 2,5-Dimethylbenzaldehyde was not detected in any of the samples. o-Tolualdehyde and m-Tolualdehyde were not detected in any of the subway trains samples while acrolein and isovaleraldehyde were presented in only a few samples.

Among the 19 carbonyls detected in the subway stations, formaldehyde was the most abundant carbonyl, followed by acetaldehyde and acetone. Their highest average concentrations were 31.7 ± 2.76, 20.6 ± 2.63, and 17.4 ± 2.29 μg m^{-3}, and accounted more than 31%, 20%, and 17% of the total carbonyl concentrations, respectively. Moreover, propionaldehyde (1.56–5.78 μg m^{-3}), butyraldehyde (1.26–8.27 μg m^{-3}), valeraldehyde (2.13–6.91 μg m^{-3}), hexaldehyde (1.14–3.66 μg m^{-3}), and nonanaldehyde (1.72–5.69 μg m^{-3}) exhibited higher concentrations. It was easy to see from Table 2 that the straight-chain compounds (i.e., C_1, C_2, C_3 and n-C_4 ~ n-C_{10}) were relatively more abundant than the aromatic carbonyls (o/m/p-tolualdehyde) and the branch-chain aldehyde (isovaleraldehyde) in the subway stations. This was not surprised, for the aromatic carbonyls such as o/m/p-tolualdehyde and 2,5-dimethylbenzaldehyde were known to come mainly from the automobile exhaustion or be products of incomplete combustion of fossil fuels [25]. Because the subway train is not driven by any of fossil fuel but the electric motive power, the levels of aromatic carbonyls were relatively low.

Unlike the subway station, only 15 out of the 20 target carbonyls were detected in the subway train samples, and acrolein, isovaleraldehyde, o-tolualdehyde, m-tolualdehyde, and 2,5-dimethylbenzaldehyde were not detected. Acetaldehyde was observed to be the dominant carbonyl species and the mean concentrations ranged from 12.6 ± 2.81 μg m^{-3} for Line 3 to 17.4 ± 3.74 μg m^{-3} for Line 2, and contributed more than 28% and 27% of the total measured carbonyl concentrations, respectively (Table 2). Formaldehyde (5.71–19.7 μg m^{-3}), acetone (4.41–13.6 μg m^{-3}), valeraldehyde (1.20–5.71 μg m^{-3})

Table 2
Carbonyls concentrations ($\mu g\,m^{-3}$) of six selected subway stations and subway trains of three lines.

Compounds	S-S($N=15$)		M-S($N=15$)		L-S($N=20$)		Line 1 ($N=10$)		Line 2 ($N=10$)		Line 3 ($N=10$)	
	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± SD	Range	Mean ± ±SD	Range	Mean ± SD	Range
Formaldehyde	21.2 ± 5.16	13.5–28.8	24.9 ± 3.96	14.7–30.2	31.7 ± 2.76	25.5–35.6	12.8 ± 2.99	5.89–18.6	14.3 ± 3.54	6.15–19.7	9.87 ± 2.11	5.71–12.6
Acetaldehyde	12.3 ± 3.58	6.46–18.4	16.3 ± 3.05	9.89–20.7	20.6 ± 2.63	16.4–24.7	15.9 ± 4.07	6.14–18.7	17.4 ± 3.74	7.91–20.9	12.6 ± 2.81	6.58–15.7
Acetone	12.1 ± 3.46	5.75–17.3	15.3 ± 2.06	10.3–18.5	17.4 ± 2.29	13.6–20.8	8.55 ± 2.52	4.41–12.6	10.2 ± 2.25	5.21–13.6	8.21 ± 1.74	4.70–10.6
Propionaldehyde	3.96 ± 1.33	1.56–5.78	3.49 ± 1.13	2.04–5.15	3.01 ± 1.14	1.48–4.80	1.98 ± 0.79	0.89–3.31	2.36 ± 0.85	0.78–3.85	1.15 ± 0.45	0.45–2.15
Acrolein	0.70 ± 0.18	0.43–0.97	0.82 ± 0.36	0.51–1.02	1.11 ± 0.39	0.91–1.27	Nd	Nd	0.26[a]	Nd–0.38	Nd	Nd
n–Butyraldehyde	3.82 ± 1.52	1.79–8.27	2.42 ± 0.92	1.26–3.80	3.26 ± 1.47	1.86–5.67	1.25 ± 0.40	0.67–2.01	2.43 ± 0.96	1.28–4.73	1.03 ± 0.31	0.67–1.66
Isovaleraldehyde	0.86 ± 0.26	0.32–1.26	0.99 ± 0.43	0.57–2.32	0.91 ± 0.38	0.31–1.33	Nd	Nd	0.19[b]	Nd–0.19	Nd	Nd
Crotonaldehyde	1.88 ± 0.36	1.31–2.45	2.55 ± 0.27	2.16–2.96	2.60 ± 0.44	1.93–3.24	0.48 ± 0.16	0.25–0.91	0.62 ± 0.21	0.32–0.88	0.37 ± 0.17	0.16–0.79
Valeraldehyde	5.05 ± 1.38	2.15–6.91	4.47 ± 1.29	2.87–6.39	3.43 ± 1.04	2.13–5.09	2.57 ± 0.77	1.31–4.12	3.78 ± 1.09	2.89–5.71	2.21 ± 0.89	1.20–3.64
Hexaldehyde	2.54 ± 0.80	1.14–3.66	2.47 ± 0.58	1.77–3.49	2.28 ± 0.41	1.37–2.78	1.25 ± 0.54	0.51–2.22	1.92 ± 0.94	0.96–3.45	0.97 ± 0.28	0.57–1.42
Cyclohexanone	1.94 ± 0.37	1.36–2.54	2.49 ± 0.35	1.64–2.88	2.18 ± 1.16	0.88–3.57	1.05 ± 0.17	0.66–1.35	1.43 ± 0.31	0.87–2.28	0.85 ± 0.20	0.47–1.10
Heptaldehyde	2.53 ± 0.79	1.12–3.61	1.17 ± 0.59	0.60–2.38	1.37 ± 0.49	0.74–2.06	1.51 ± 0.35	0.75–3.69	1.83 ± 0.78	0.59–2.87	1.12 ±0.40	0.62–1.75
Octylaldehyde	2.69 ± 0.54	1.91–3.57	2.65 ± 0.87	1.55–4.05	1.66 ± 0.45	1.15–2.44	1.28 ± 0.27	0.81–1.77	1.47 ± 0.55	0.51–2.08	1.19 ± 0.31	0.59–2.13
Benzaldehyde	1.77 ± 0.53	1.94–2.62	2.61 ± 0.67	1.63–3.99	2.02 ± 0.51	1.25–2.56	1.43 ± 0.50	1.16–2.54	1.62 ± 0.66	0.36–2.16	1.40 ± 0.42	0.81–2.25
Nonanaldehyde	3.65 ± 0.61	2.69–4.67	3.77 ± 1.33	1.91–5.69	2.57 ± 0.47	1.72–3.11	1.91 ± 0.74	1.46–3.79	2.36 ± 1.02	1.13–4.25	2.21 ± 0.87	1.09–3.76
o–Tolualdehyde	0.79 ± 0.21	0.33–1.11	0.71 ± 0.28	0.50–1.33	0.49 ± 0.13	0.25–0.65	Nd	Nd	Nd	Nd	Nd	Nd
m-Tolualdehyde	0.45 ± 0.12	0.19–0.64	0.69 ± 0.11	0.51–0.84	0.71 ± 0.12	0.53–0.92	Nd	Nd	Nd	Nd	Nd	Nd
p-Tolualdehyde	0.90 ± 0.24	0.381.27	1.2 ± 0.31	0.88–1.32	1.16 ± 0.26	0.64–1.46	0.27[c]	Nd –0.41	0.32[d]	Nd–0.59	Nd	Nd
Decylaldehyde	1.11 ± 0.19	0.82–1.43	2.01 ± 0.48	1.59–3.13	1.98 ± 0.55	1.01–2.72	1.07 ± 0.44	0.41–2.14	1.35 ± 0.46	0.77–2.48	0.54 ± 0.27	0.19–0.89
2,5-Dimethylbenzaldehyde	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd
Total	80.2 ± 21. 6	45.2–115	91.1 ± 19.1	56.8–120	101 ± 17.1	73.7–124	53.3 ± 14.7	25.4–78.2	63.8 ± 17.4	29.7–90.9	43.7 ± 11.2	23.8–60.4

N: number of samples; Mean: arithmetic mean; SD: standard deviation; Nd: not detected; S-S: small scale station, including Shanghai Circus World station (S1) and North Zhongshan Road station (S2); M-S: medium scale station, including Xujiahui station (S3) and Lujiazui station (S4); L-S: large scale station, including People Square station (S5) and Zhongshan Park station (S6).

[a] Two samples average.

[b] Only one sample.

[c] Three samples average.

[d] Four samples average.

Table 3
Mean concentration ($\mu g\,m^{-3}$) of outdoor air, *I*/*O* ratios and correlation coefficients for some carbonyls in the subway stations.

Compounds	Outdoor air concentrations		*I*/*O* ratio		Pearson coefficient ($n = 50$)	
	Mean[a]	Range[a]	Mean[b]	Range[b]	$R_{(formaldehyde)}$[c]	$R_{(acetaldehyde)}$[c]
Formaldehyde	10.78 ± 2.38	7.59–15.49	2.56 ± 1.86	1.07–4.19	1.00	0.63[d]
Acetaldehyde	6.87 ± 1.81	3.03–9.16	3.44 ± 1.96	1.56–7.43	0.63[d]	1.00
Acetone	5.01 ± 1.54	2.84–8.47	3.27 ± 1.38	1.79–5.87	0.41[d]	0.56[d]
Propionaldehyde	1.73 ± 1.21	0.51–4.52	2.38 ± 0.84	1.12–3.57	0.32	0.45[d]
Acrolein	0.53 ± 0.21	0.31–0.90	1.84 ± 0.60	1.09–2.62	0.27	0.23
n-Butyraldehyde	1.97 ± 0.98	1.01–4.08	1.60 ± 0.64	1.03–3.47	0.36[d]	0.39
Isovaleraldehyde	0.56 ± 0.27	0.29–1.02	1.82 ± 0.89	0.94–3.71	−0.08	0.09
Crotonaldehyde	1.35 ± 0.46	0.47–2.41	1.92 ± 0.87	0.97–4.29	0.27	0.13
Valeraldehyde	2.53 ± 1.08	1.25–5.07	1.85 ± 0.56	1.12–2.96	0.21	0.26
Hexaldehyde	1.72 ± 0.80	0.68–3.28	1.65 ± 0.73	0.97–2.90	0.14	0.15
Cyclohexanone	1.31 ± 0.52	0.54–2.44	1.78 ± 0.66	0.91–2.98	0.19	0.10
Heptaldehyde	1.32 ± 1.08	0.25–3.47	1.65 ± 0.73	0.98–2.89	−0.02	0.08
Octylaldehyde	1.65 ± 0.71	0.47–2.99	1.48 ± 0.49	1.04–2.63	0.05	−0.12
Benzaldehyde	2.60 ± 0.41	1.99–3.45	0.96 ± 0.22	0.68–1.41	0.18	0.09
Nonanaldehyde	2.24 ± 1.34	0.54–4.91	1.81 ± 0.80	0.83–3.40	0.23	0.17
o-Tolualdehyde	1.12 ± 0.28	0.75–1.82	0.65 ± 0.27	0.31–1.28	0.16	0.21
m-Tolualdehyde	1.16 ± 0.27	0.74–1.78	0.57 ± 0.17	0.37–0.87	0.18	0.13
p-Tolualdehyde	1.29 ± 0.35	1.10–2.23	0.94 ± 0.32	0.56–1.53	0.09	0.15
Decylaldehyde	1.13 ± 0.44	0.42–1.78	1.82 ± 1.11	0.97–4.81	−0.11	0.18
2,5-Dimethylbenzaldehyde	0.78 ± 0.32	0.36–1.41	–	–	–	–
Total	47.6 ± 16.5	24.9–80.4	34.2 ± 15.3	18.2–63.1	–	–

Mean: arithmetic mean; SD: standard deviation.
[a] The mean ± SD and the rang of concentration ($\mu g\,m^{-3}$) of outdoor levels ($n = 12$).
[b] The mean ± SD and the rang of I/O ratios ($n = 12$), *I*/*O*: indoor (subway stations)/outdoor (exit).
[c] Pearson coefficient ($n = 50$).
[d] 99% confidence levels.

and nonanaldehyde (1.09–4.25 $\mu g\,m^{-3}$) were the next four abundant carbonyl compounds. The order of total average carbonyl concentrations for the subway stations was large scale stations ($101 \pm 17.1\ \mu g\,m^{-3}$) > medium scale station ($91.1 \pm 19.1\ \mu g\,m^{-3}$) > small scale station ($80.2 \pm 21.6\ \mu g\,m^{-3}$), while for the subway trains was Line 2 ($63.8 \pm 17.4\ \mu g\,m^{-3}$) > Line 1 ($53.3 \pm 14.7\ \mu g\,m^{-3}$) > Line 3 ($43.7 \pm 11.2\ \mu g\,m^{-3}$). The results showed that total carbonyl concentrations in the subway stations were about 1.4–2.5 times higher than in the subway trains. In addition, carbonyl levels in-subway trains of Line 2, with a whole of underground track, had the highest average total carbonyl concentration, while in Line 3, with a whole of overground track, had the lowest average total carbonyl concentration.

Carbonyl compounds presented in the indoor air are thought to be resulting from the indoor emissions, indoor chemical formation and outdoor infiltration [26]. Lower correlations were found between indoor concentration of formaldehyde, acetaldehyde and most other carbonyls, especially for C_4–C_{10} carbonyl compounds ($R < 0.4$, Table 3), which possibly proved the complex sources of the carbonyls in the subway station. Since the subway trains are driven by electric motive power, as mentioned above, the high levels of aldehydes might come from the indoor sources, such as wall coverings of station building, decorating materials both for station and train, also outdoor air by ventilation, and even human beings [26–28]. Acetaldehyde is a product of the human metabolism and present in human expired air [26,28], especially after alcohol consumption or smoke [29]. Acetone had long lifetime in the atmosphere and could also be produced by human metabolism [28,30]. Relative good correlations were found between formaldehyde and acetaldehyde ($R = 0.63$, Table 3), acetone and acetaldehyde ($R = 0.56$) in-subway stations, which mean that formaldehyde and acetaldehyde shared the common source, probably from outdoor air, while acetone and acetaldehyde also have similar sources, such as the expired air from human being.

Ventilation system is also one of the important factors to affect the carbonyls levels in the indoor environment [31,32]. Lower carbonyl concentrations were measured in-subway trains for some carbonyls (when $I/O < 1$) was that the carbonyls are diluted by the ventilation system because inside the moving subway trains the ventilation is relatively higher than in the subway stations (the mean airflow measured in the subway trains was about 0.8 $m\,s^{-1}$ and was up to 2.6 $m\,s^{-1}$ when sampling by a portable wind velocity indicator, Kestrel 4000, USA). The carbonyl concentrations were higher inside the subway stations than that outside the subway station in Line 3 (Table 3) although the subway trains are overground.

Table 4
Correlation between the concentrations of ozone and eight abundant carbonyls both in-subway stations and in-subway trains.

Carbonyl compounds	Subway stations ($n = 50$, $p < 0.01$)		Subway trains ($n = 24$, $p < 0.01$)	
	R	SD	*R*	SD
Formaldehyde	0.83	2.54	0.53	2.81
Acetaldehyde	0.72	1.65	0.41	2.19
Acetone	0.79	0.83	0.33	1.03
Propionaldehyde	0.48	0.48	0.29	0.36
n-Butyraldehyde	0.52	0.45	0.34	0.26
Valeraldehyde	0.25	0.36	0.17	0.24
Hexaldehyde	0.16	0.31	0.14	0.16
Nonanaldehyde	0.13	0.58	0.12	0.15

R: Pearson coefficient.

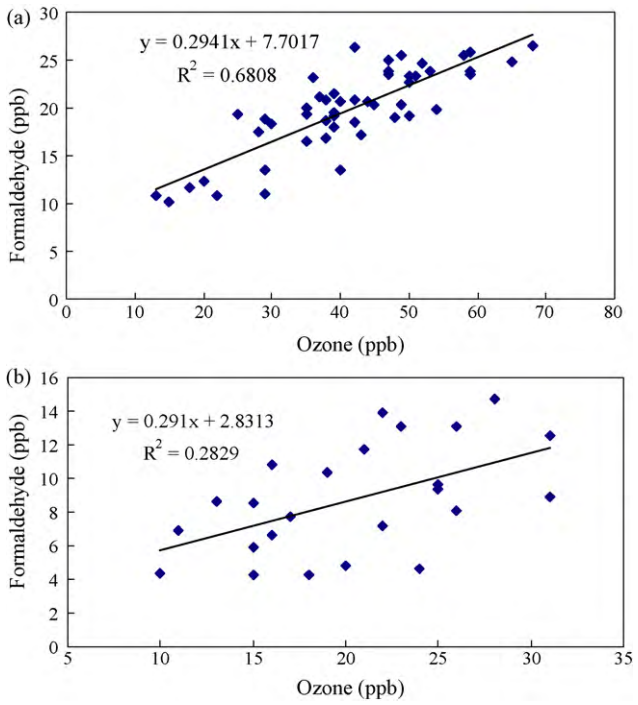

Fig. 2. Correlation between concentrations of formaldehyde and ozone.

The correlation between ozone and formaldehyde concentrations was shown in Fig. 2 and Table 4. It was found that there was a significant relationship between the concentrations of formaldehyde and ozone in the subway stations ($R = 0.81$, $p < 0.01$, Fig. 2(a)), while relatively lower correlation in the subway train ($R = 0.53$, $p < 0.01$, Fig. 2(b)). Table 4 showed the correlation between the eight most abundant carbonyl compounds and ozone both in the subway stations and in the subway trains. There were good correlations between the concentrations of the low molecular-weight carbonyl compounds ($<C_5$) and ozone in the subway stations ($R > 0.5$, $p < 0.01$), while the high molecular-weight carbonyl compounds (C_5–C_{10}) exhibited poor correlation. The high correlation between the concentration of the low molecular-weight ($<C_5$) carbonyl compounds and ozone in the subway stations showed that they may be from common sources (e.g., outdoor air by ventilation). Compared with the subway station, the correlations (R) between the concentrations of carbonyls and ozone in the subway train were relatively low for all carbonyl compounds. This implied that carbonyls in the subway trains may have more emission sources, such as the decorating materials inside the subway trains and the direct emissions from the passengers.

3.2. Diurnal variations of carbonyls

The diurnal sampling was performed during the service time of the subway station (between 6:30 a.m. and 10:30 p.m.). The sampling was divided into five periods: the morning peak hour, morning hour, afternoon hour, the evening peak hour, and evening hour. The eight most abundant carbonyl compounds, including formaldehyde, acetaldehyde, acetone, propionaldehyde, n-butylaldehyde, valeraldehyde, hexaldehyde, and nonanaldehyde, were shown in Fig. 3.

Fig. 3 presented diurnal variations of eight carbonyl compounds from 06:30 to 22:30. In the subway station (Fig. 3(a and b)) the highest carbonyls levels were observed at the morning peak hour (06:30–09:30), while acetaldehyde, the second abun-

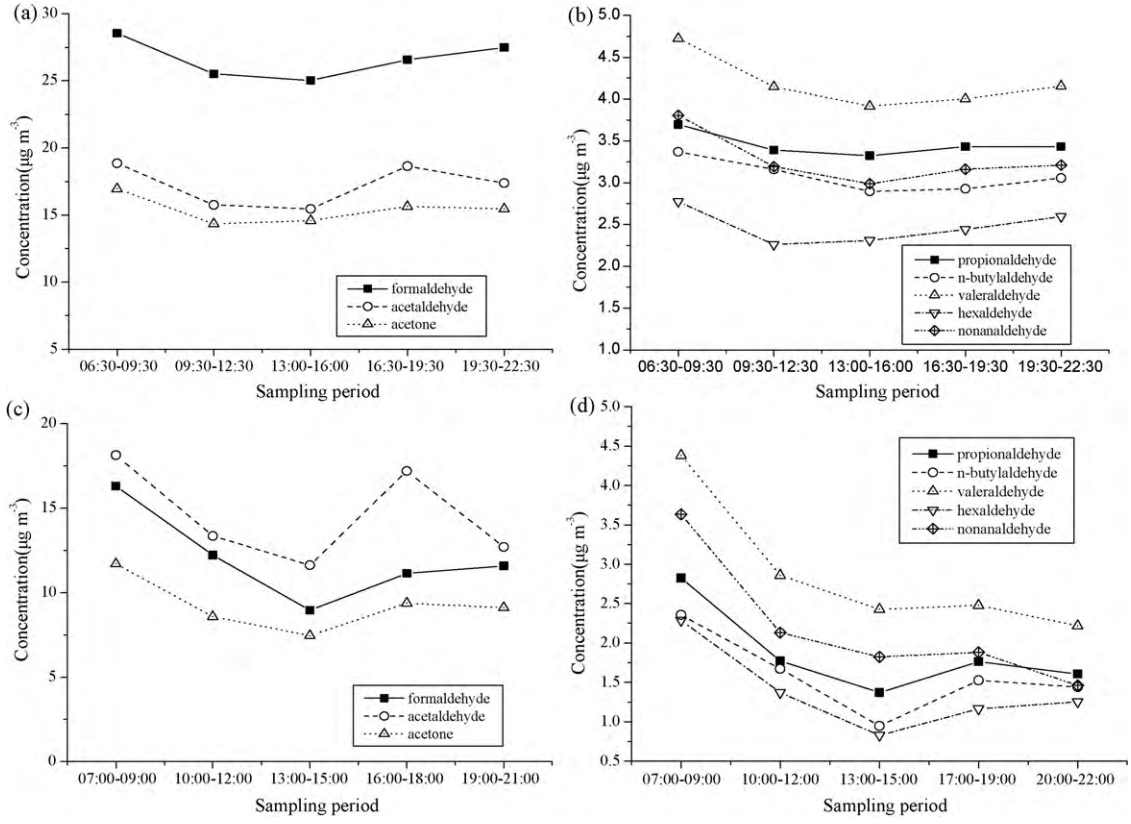

Fig. 3. Diurnal variations of mean concentrations of the eight most abundant carbonyl compounds (including formaldehyde, acetaldehyde, acetone, propionaldehyde, n-butylaldehyde, valeraldehyde, hexaldehyde and nonanaldehyde) in the subway stations and in-subway trains.

dant compounds, had a obvious bimodal variation with a higher peak at the morning peak hour (06:30–09:30) and a lower peak at the evening peak hour (16:30–19:30). Except acetaldehyde, seven other carbonyls (including formaldehyde, acetone, propionaldehyde, n-butylaldehyde, valeraldehyde, hexaldehyde, and nonanaldehyde) displayed similar diurnal variations both in the subway station and subway train. However, no prominent variations were found before and after the evening peak hour in the subway station (Fig. 3(a and b)). This is similar with the diurnal variations of carbonyls in Shanghai urban air [33], which implied that carbonyl concentrations in the subway stations might be significantly affected by outdoor air. Similar to the subway station, all the carbonyl concentrations in-subway train (Fig. 3(c and d)) showed the highest levels at the morning peak hour and then appeared descending trend during day time. Higher concentrations of acetaldehyde in the subway train were found both at the morning and evening peak hour. Moreover, the concentration of acetaldehyde had noticeable changes before and after the evening peak hour in the subway trains (Fig. 3c). This phenomenon proved again that acetaldehyde could be produced by human metabolism. This result was consistent with previous study by Pang and Mu [30], which reported that there were significant differences in acetaldehyde concentration as commuter number increased from several to about 300 of commuters in a subway cabin in Beijing.

3.3. Comparison of indoor results with other literatures

There is little information regarding indoor air concentrations of carbonyls in the subway station. Table 5 listed the results of the present study and other studies in public traffic building and other traffic modes such as bus, car, and railway trains. It can be seen from Table 5 that the levels of formaldehyde and acetaldehyde in-subway train were lower than in other traffic modes in general. Based on the in-subway train measurements, the acetaldehyde levels of the present study were close to the studies by Pang and Mu [30], but formaldehyde levels were lower than the studies by Shiohara et al. [34] and Pang and Mu [30]. The differences may be due to the inconsistency of field study designs, actual subway trace, background levels in stations, ventilation condition and other conditions [6,35]. In addition, for the commuters, the formaldehyde exposure level of railway was nearly fourfold of those in the subway. Although the subway train was the relatively safe public traffic mode, the levels of formaldehyde and acetaldehyde in-subway station were still much higher than in the hall of train station and airport [16] where the passengers would spend most of time for commuting.

3.4. Indoor/outdoor ratios and comparison with indoor levels

The mean concentrations of carbonyls outside the subway station were listed in Table 3. All the twenty target carbonyls were detected in the outdoor air samples. Formaldehyde, acetaldehyde, and acetone were the three most abundant carbonyls. Their mean concentrations were 10.8 ± 2.38, 6.87 ± 1.81, and $5.01 \pm 1.54\ \mu g\ m^{-3}$, respectively. Comparison of the indoor and outdoor carbonyl concentrations found to be "indoor > outdoor" for almost each measurement pair. Mean concentrations of carbonyl in outdoor air and indoor/outdoor aldehydes concentrations (I/O ratios) were shown in Table 3. It could be seen that with the exceptions of benzaldehyde, o/m/p-tolualdehyde ($I/O < 1$), all the other identified carbonyl compounds had mean $I/O > 1$. The higher indoor carbonyl concentrations may be resulted from complex chemical and physical processes which determine the emission, generation and accumulation of the carbonyls in the indoor environment. For benzaldehyde and o/m/p-tolualdehyde, which are mainly from outdoor source (e.g. vehicle exhaust).

3.5. Personal exposure and cancer risk

The individual (i) exposures (E) and cancer risk to the indoor carbonyls were calculated from the equation in Guidelines for Exposure Assessment [36]:

$$E_i = C_j \mathrm{IR}_i t_{ij}$$

where C is the concentration of the pollutant ($\mu g\ m^{-3}$), IR is the inhalation rate ($m^3\ h^{-1}$), t is the exposure time ($h\ day^{-1}$), and j is the microenvironment.

In the current study, the indoor carbonyls of six subway stations and the in-subway train only for Line 2 (with a whole of underground track) were selected to calculate the exposure (E), of which the mean exposure time (t) of 2 h was considered for the commuters to stay in the subway both for waiting on the platform or getting on the train everyday. The mean and the 95th percentile results for indoor exposure were estimated (Table 6) in comparison with some other public places. Results showed that the exposure for formaldehyde and acetaldehyde in the subway was similar to the office in Mexico City [15] and lower than ballrooms [13] and hospital in Guangzhou [12,37]. However, it should be noted that the exposures of the current study were calculated only based on the 2 h of mean exposure time for the commuters. If exposure time was longer, especially to the subway workers, the individual exposures would be three or four times of the current results (based on their working time in the station). According to a 2008 government

Table 5
Comparison of mean concentrations ($\mu g\ m^{-3}$) of the most abundant carbonyls with other traffic modes.

Location	Sampling site	HCHO	CH_3CHO	Reference
Shanghai, China	Platform of subway station	25.9	16.4	Current study
	In-subway train	12.3	15.3	
Strasbourg, France	Hall of train station	7.0	1.6	Marchand et al. [16]
	Hall of airport	10.8	3.5	
Mexico City, Mexico	In-microbus (22-seater)	40.2	–	Shiohara et al [34]
	In-bus	24.7	–	
	In-subway train	19.4	–	
Beijing, China	In-taxi (Xiali)	28	28	Pang and Mu [30]
	In-bus	24	20	
	In-subway train	19.0	14.0	
Taegu, Korea	In-car	25.6[a]	13.8[a]	Jo and Lee [31]
	In-bus	26.9[a]	14.7[a]	

[a] The unit of ppb in the original literature was converted to be the unit of $\mu g\ m^{-3}$.

Table 6
Comparison of exposure risks of formaldehyde and acetaldehyde in the indoor air of public places.

Parameter	Formaldehyde				Acetaldehyde			
	Arithmetic mean	95th percentile	Risk		Arithmetic mean	95th percentile	Risk	
			Mean	95th percentile			Mean	95th percentile
Office[a]								
C ($\mu g\,m^{-3}$)	26.2	34.4	3.4×10^{-4}	4.5×10^{-4}	19.3	32.7	3.4×10^{-5}	6.1×10^{-5}
E ($\mu g\,day^{-1}$)	132	173	–	–	97	165		
Hospital[b]								
C ($\mu g\,m^{-3}$)	8.3	10.9	1.1×10^{-4}	1.4×10^{-4}	12.9	20.3	2.8×10^{-5}	4.5×10^{-5}
E ($\mu g\,day^{-1}$)	41.8	54.9	–	–	65	102	–	–
Ballroom[c]								
C ($\mu g\,m^{-3}$)	33.1	55	4.4×10^{-4}	7.2×10^{-4}	100.1	225.7	22.6×10^{-5}	51×10^{-5}
E ($\mu g\,day^{-1}$)	124	209	–	–	378	853	–	–
Subway[d]								
C ($\mu g\,m^{-3}$)	24.5	34.2	3.2×10^{-4}	4.4×10^{-4}	17.0	24.2	3.7×10^{-5}	5.3×10^{-5}
E ($\mu g\,day^{-1}$)	30.9	43.0	–	–	21.4	30.5	–	–

Inspire rate is $0.63\,m^3\,h^{-1}$ for exposure calculation and the inhalation unit risk estimates of formaldehyde and acetaldehyde were 1.3×10^{-5} and 2.2×10^{-6} $(\mu g\,m^{-3})^{-1}$, respectively according to EPA exposure factors [36].

[a] Baez et al. [15].
[b] Lu et al. [37].
[c] Feng et al. [13].
[d] Current study, indoor carbonyl exposures of six subway station and subway train of Line 2.

report, there will be more than 20,000 subway works in Shanghai at 2010. For this great number of workers, the negative effects on human health from the indoor carbonyls, should be given more concern [10,25].

4. Conclusion

This study measured indoor and outdoor carbonyl levels of six subway stations and the in-subway trains of three lines. Formaldehyde was the most abundant carbonyl in the subway station, while acetaldehyde was the dominant carbonyl species in-subway trains. Carbonyl concentrations in the subway stations were relatively higher than those in in-subway trains which were determined to a large extent by the actual routine routes of subway lines. Good correlations were found between the concentration of the low molecular-weight carbonyl compounds ($<C_5$) and ozone in the subway stations. The diurnal variations both in the subway station and in-subway train showed that the carbonyl concentrations were significantly higher in the morning rush hour and then appeared descending trend during day time, which is similar with the ambient air. The *I*/*O* ratios were greater than 1 for most of carbonyl compounds. All the results showed that the concentrations of carbonyls were affected significantly by outdoor air. Although the subway train was considered to be the safe mode for commuting by comparing with other public traffic modes such as bus, taxi or train, the carbonyl exposure for people in the subway station should not be ignored. The current results showed that the underground subway stations in shanghai commuting conditions were not only an important microenvironment for exposure to formaldehyde and acetaldehyde, but also clearly a risk of carbonyl exposure for people who worked in the subway stations or taken on subway train for commuting every day.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (grants 40773047 and 40973071), Shanghai Rising-Star Program (09QA1402100), Shanghai Leading Academic Disciplines (S30109) and Earmarked Fund of the State Key Laboratory of Organic Geochemistry (OGL-200705).

References

[1] I. Salma, T. Weidinger, W. Maenhaut, Time-resolved mass concentration, composition and sources of aerosol particles in a metropolitan underground railway station, Atmos. Environ. 41 (2007) 8391–8405.
[2] J.E. Gomez-Perales, R.N. Colvile, M.J. Nieuwenhuijsen, A. Fernandez-Bremauntz, V.J. Gutierrez-Avedoy, V.H. Paramo-Figueroa, S. Blanco-Jimenez, E. Bueno-Lopez, F. Mandujano, R. Bernabe-Cabanillas, E. Ortiz-Segovia, Commuters' exposure to PM2.5, CO, and benzene in public transport in the metropolitan area of Mexico City, Atmos. Environ. 38 (2004) 1219–1229.
[3] H.L. Karlsson, A.G. Ljungman, J. Lindbom, L. Moller, Comparison of genotoxic and inflammatory effects of particles generated by wood combustion, a road simulator and collected from street and subway, Toxicol. Lett. 165 (2006) 203–211.
[4] K.Y. Kim, Y.S. Kim, Y.M. Roh, C.M. Lee, C.N. Kim, Spatial distribution of particulate matter (PM10 and PM2.5) in Seoul Metropolitan Subway stations, J. Hazard. Mater. 154 (2008) 440–443.
[5] D.U. Park, K.C. Ha, Characteristics of PM10, PM2.5, CO_2 and CO monitored in interiors and platforms of subway train in Seoul, Korea, Environ. Int. 34 (2008) 629–634.
[6] L.Y. Chan, W.L. Lau, X.M. Wang, J.H. Tang, Preliminary measurements of aromatic VOCs in public transportation modes in Guangzhou, China, Environ. Int. 29 (2003) 429–435.
[7] N. Boudia, R. Halley, G. Kennedy, J. Lambert, L. Gareau, J. Zayed, Manganese concentrations in the air of the Montreal (Canada) subway in relation to surface automobile traffic density, Sci. Total. Environ. 366 (2006) 143–147.
[8] J.H. Cho, K.H. Min, N.W. Paik, Temporal variation of airborne fungi concentrations and related factors in subway stations in Seoul, Korea, Int. J Hyg. Environ. Health 209 (2006) 249–255.
[9] E. Grosjean, D. Grosjean, Carbonyl collection efficiency of the DNPH-coated C-18 cartridge in dry air and in humid air, Environ. Sci. Technol. 30 (1996) 859–863.
[10] E. Grosjean, D. Grosjean, Carbonyl products of the gas-phase reaction of ozone with 1-alkenes, Atmos. Environ. 30 (1996) 4107–4113.
[11] M. Possanzini, V. Di Palo, Simultaneous determination of HCHO, CH_3CHO and O-x in ambient air by hydrazine reagent and HPLC, Ann. Chim. (Rome) 93 (2003) 149–156.
[12] Y. Feng, S. Wen, Y. Chen, X. Wang, H. Lu, X. Bi, G. Sheng, J. Fu, Ambient levels of carbonyl compounds and their sources in Guangzhou, China, Atmos. Environ. 39 (2005) 1789–1800.
[13] Y. Feng, S. Wen, Y.X. Wang, G. Sheng, Q. He, J. Tang, J. Fu, Indoor and outdoor carbonyl compounds in the hotel ballrooms in Guangzhou, China, Atmos. Environ. 38 (2004) 103–112.
[14] B. Wang, S.C. Lee, K.F. Ho, Characteristics of carbonyls: concentrations and source strengths for indoor and outdoor residential microenvironments in China, Atmos. Environ. 41 (2007) 2851–2861.
[15] A. Baez, H. Padilla, R. Garcia, M.D. Torres, I. Rosas, R. Belmont, Carbonyl levels in indoor and outdoor air in Mexico City and Xalapa, Mexico, Sci. Total Environ. 302 (2003) 211–226.
[16] C. Marchand, B. Buillot, S. Le Calve, P. Mirabel, Aldehyde measurements in indoor environments in Strasbourg (France), Atmos. Environ. 40 (2006) 1336–1345.
[17] S.S.H. Ho, J.Z. Yu, Concentrations of formaldehyde and other carbonyls in environments affected by incense burning, J. Environ. Monit. 4 (2002) 728–733.

[18] H. Lü, Q. Cai, S. Wen, Y. Chi, S. Guo, G. Sheng, J. Fu, A. Katsoyiannis, Carbonyl compounds and BTEX in the special rooms of hospital in Guangzhou, China, J. Hazard. Mater. 178 (2010) 673–679.
[19] P. Jenkins, T. Phillips, E. Mulberg, S. Hui, Activity patterns of Californians: use of and proximity to indoor pollutant sources, Atmos. Environ. 26 (1992) 2141–2148.
[20] Eurostat, How Europeans Spend Their Time – Everyday Life of Women and Men. Data 1998–2002, Office for Official Publications of the European Communities, Bernan Press, Luxembourg, 2004.
[21] M. Possanzini, V. Dipalo, M. Petricca, R. Fratarcangeli, D. Brocco, Measurements of lower carbonyls in Rome ambient air, Atmos. Environ. 30 (1996) 3757–3764.
[22] S.D. Richardson, T.V. Caughran, T. Poiger, Y.B. Guo, F.G. Crumley, Application of DNPH derivatization with LC/MS to the identification of polar carbonyl disinfection by-products in drinking water, Ozone Sci. Eng. 22 (2000) 653–675.
[23] S.S.H. Ho, J.Z. Yu, Determination of airborne carbonyls: comparison of a thermal desorption/GC method with the standard DNPH/HPLC method, Environ. Sci. Technol. 38 (2004) 862–870.
[24] J. Li, Y. Feng, C. Xie, J. Huang, J.Z. Yu, J. Feng, G. Sheng, J. Fu, M. Wu, Determination of gaseous carbonyl compounds by their pentafluorophenyl hydrazones with gas chromatography/mass spectrometry, Anal. Chim. Acta 635 (2009) 84–93.
[25] M. Possanzini, V. Di Palo, E. Brancaleoni, M. Frattoni, P. Ciccioli, A train of carbon and DNPH-coated cartridges for the determination of carbonyls from C-1 to C-12 in air and emission samples, Atmos. Environ. 34 (2000) 5311–5318.
[26] J. Zhang, Q. He, P.J. Lioy, Characteristics of aldehydes: concentrations, sources, and exposure for indoor and outdoor residential microenvironment, Environ. Sci. Technol. 28 (1994) 146–152.
[27] J.P. Conkle, B.J. Camp, B.E. Welch, Trace composition of human respiratory gas, Arch. Environ. Health 30 (1975) 290–295.
[28] C.J. Weschler, H.C. Shields, The effects of ventilation, filtration, and outdoor air on indoor air at telephone office building, Environ. Int. 15 (1989) 593–604.
[29] A.W. Jones, Measuring and reporting the concentration of acetaldehyde in human breath, Alcohol Alcohol. 30 (1995) 271–285.
[30] X. Pang, Y. Mu, Characteristics of carbonyl compounds in public vehicles of Beijing city: concentrations, sources, and personal exposures, Atmos. Environ. 41 (2007) 1819–1824.
[31] W.K. Jo, J.W. Lee, In-vehicle exposure to aldehydes while commuting on real commuter routes in a Korean urban area, Environ. Res. 88 (2002) 44–51.
[32] A.T. Chan, Commuter exposure and indoor-outdoor relationships of carbon oxides in buses in Hong Kong, Atmos. Environ. 37 (2003) 3809–3815.
[33] J. Huang, Y. Feng, J. Li, B. Xiong, J. Feng, S. Wen, G. Sheng, J. Fu, M. Wu, Characteristics of carbonyl compounds in ambient air of Shanghai, China, J. Atmos. Chem. 61 (2009) 1–20.
[34] N. Shiohara, A.A. Fernandez-Bremauntz, S.B. Jimenez, Y. Yanagisawa, The commuters' exposure to volatile chemicals and carcinogenic risk in Mexico City, Atmos. Environ. 39 (2005) 3481–3489.
[35] W.K. Jo, K.H. Park, Commuter exposure to volatile organic compounds under different driving conditions, Atmos. Environ. 33 (1999) 409–417.
[36] U.S. Environmental Protection Agency, Guidelines for exposure assessment, EPA 600Z-92y001, Office of Research Development, Office of Health and Environmental Assessment, Washington, DC, 1992.
[37] H. Lü, S. Wen, Y. Feng, X. Wang, X. Bi, G. Sheng, J. Fu, Indoor and outdoor carbonyl compounds and BTEX in the hospitals of Guangzhou, China, Sci. Total Environ. 368 (2006) 574–584.