Journal of Hazardous Materials 164 (2009) 700–706

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

Levels and health risks of carbonyl compounds in selected public places in Hangzhou, China

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ARTICLE INFO

Article history:
Received 10 June 2008
Received in revised form 15 August 2008
Accepted 18 August 2008
Available online 4 September 2008

Keywords:
Carbonyl compounds
Indoor air
Public place
Health risk

ABSTRACT

The concentrations of six carbonyl compounds in indoor air were measured for selected public places in Hangzhou, including shopping centers, supermarkets, furniture store, inter-city bus stations, railway stations and cinemas. In indoor air of the public places, the mean concentration was 146.5 $\mu g/m^3$ for total carbonyls, in which formaldehyde was found to be the most abundant carbonyls with an average value of 90.6 $\mu g/m^3$ and followed by acetone and acetaldehyde. Among the selected public places, the furniture store presented the highest carbonyl concentrations in the indoor air, followed by shopping centers, supermarkets, cinemas, while the railway stations and inter-city bus stations presented relatively lower carbonyl concentrations. Carbonyl concentrations in indoor air for the different areas of shopping centers and supermarkets were also investigated. The results showed that the highest carbonyl concentrations were found in restaurant and bedclothes areas for shopping centers and in the cooked food areas for supermarkets. The average ratios of the indoor/outdoor (I/O) for carbonyl concentrations were greater than 1, which indicated that the indoor sources significantly contributed to carbonyls, such as indoor materials and anthropogenic activities. Preliminary estimate of the health risk for staffs, customers and passengers in public places was discussed.

1. Introduction

Carbonyl compounds are ubiquitous in ambient air and well known for their adverse effects on human health [1]. The most frequently adverse impacts of them on human health are eye and lung irritations [2]. Formaldehyde is classified in Group 1 (human carcinogen) by the International Agency for Research on Cancer (IARC) for its carcinogenicity [3] and acetaldehyde is classified as a suspected carcinogen [4,5].

The pollution levels, possible sources and human exposure of carbonyls in the indoor environment have received increasing attention in recent years [3–15]. The pollution levels of carbonyls were measured in indoor and outdoor air of residences in New Jersey. The results showed that the indoor/outdoor ratios (I/O) > 1, indicating that the presence of the indoor sources [4]. The investigation of carbonyl levels in hotel ballrooms of Guangzhou indicated that formaldehyde and acetaldehyde were the most abundant carbonyls, and there existed a strong correlation between formaldehyde and acetaldehyde [9]. Similar investigations were also carried out in offices, academies and hospitals [5,10–12]. Besides, researches showed that direct emission from indoor materials and other anthropogenic sources, e.g. tobacco smoke and cooking, also significantly contributed to carbonyls [6,7]. Regulations and guidelines for the use and production of formaldehyde and acetaldehyde have been established by the Occupational Safety and Health Administration (OSHA). The permissible exposure limit (PEL) at 0.75 ppm as an 8-h time-weighted average (TWA) and 2 ppm in 15 min as a short-term exposure limit (STEL) has been determined for formaldehyde [15]. For acetaldehyde, the legal airborne PEL is 200 ppm averaged over an 8-h work shift [15].

Nowadays, with the development of the economy, leisure and entertainment activities have become more and more popular in China. During holidays, visitors and customers reach ten of thousands person-time in public places for leisure and entertainment. Meanwhile, decoration and refurbishment have been widely used in public places to improve the indoor environment and attract the customers. In those public places, some harmful compounds, especially carbonyls, are emitted from decorating- and refurbishing-materials and tend to accumulate in indoor air due to low air exchange rate. To our knowledge, most of the previous researches were focused on the carbonyl levels in residences and offices. However, the data of the carbonyl concentrations in the indoor air of the public places for entertainment and leisure

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doi:10.1016/j.jhazmat.2008.08.094

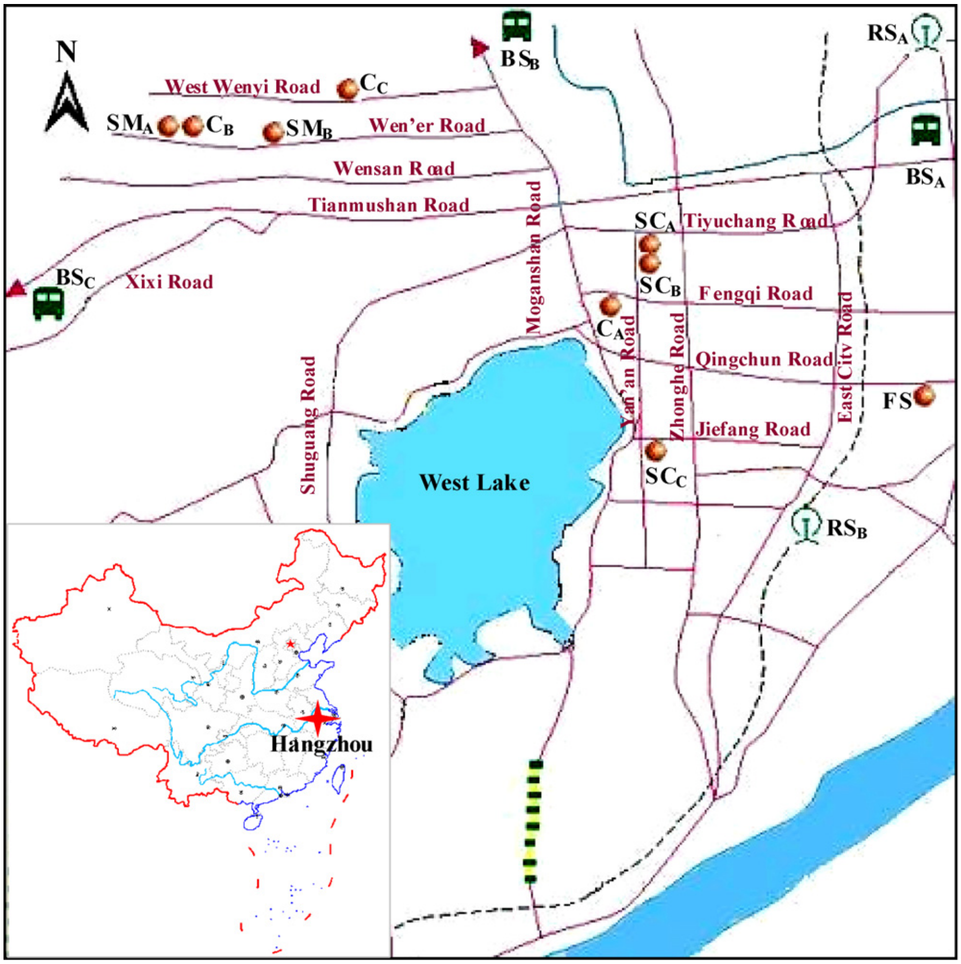

Fig. 1. Sampling sites in Hangzhou (SC: shopping center; SM: supermarket; FS: furniture store; BS: bus station; RS: railway station; C: cinema).

in China, such as shopping centers, supermarkets and cinemas, are not available.

In the present study, systematic measurements of six carbonyls were carried out in indoor air of selected public places in Hangzhou, including three shopping centers, two supermarkets, one furniture store, three inter-city bus stations, two railway stations and three cinemas. The possible sources of carbonyl compounds inside public places were discussed in detail. In addition, carbonyl levels in different areas of shopping centers and supermarkets were investigated and the main carbonyl sources were analyzed. Based on these results, the public and occupational health risks of carbonyls at these public places were discussed.

2. Materials and methods

2.1. Sampling sites

Indoor air samplings were conducted in three shopping centers, two supermarkets, one furniture store, three inter-city bus stations, two railway stations, three cinemas and different shopping areas for shopping centers and supermarkets. The sampling sites were described in Fig. 1 and Table 1. Indoor air samples were collected during the opening time of the selected public places from March to April 2006 in Hangzhou. The sampling period ranged from 3 to 6 h. The indoor air samples were also taken in different shopping areas for shopping centers and supermarkets. Outdoor air samples were taken simultaneously outside shopping centers, supermarkets and furniture store. The outdoor sampling sites were immediate outside of the selected places, but far away from the doors and windows to avoid the influences of indoor air. The air samples were taken in the middle of the sampling area at approximately 1.50 m above the floor.

2.2. Chemicals and materials

The calibration standards (Supelco, USA) contained 2,4-dinitrophenylhydrazine (DNPH) derivatives of formaldehyde, acetaldehyde, acetone, propionaldehyde, crotonaldehyde and butyraldehyde. The DNPH was further purified by recrystallized three times in acetonitrile. Silica gel was 60–80 mesh. All organic solvents were HPLC grade and water was ultrapure grade.

2.3. Sampling and analytical methods

The whole method was based on EPA method TO-11A [16]. The sampling cartridges consist of glass tubes (15 cm length, 2 cm i.d.), which were filled with silica gel coated with a diluted 2,4-DNPH acidified solution. The solution was prepared as follows: 0.1357 mg purified DNPH was dissolved in 200 mL acetonitrile. Then the pH of the solution was adjusted to 3 with phosphoric acid.

Air samples were taken by drawing the air with the air samplers (DDY-1.5, Xingyu, China). The sampling rate was 0.5 L/min. An ozone scrubber was connected to the upstream end of the cartridge to avoid ozone interference. After sampling, each cartridge

Table 1
The description of the selected public places

Public place	Ventilation	Nearby environment
Shopping center A	Air conditioner	Commercial area with high traffic density
Shopping center B	Air conditioner	Commercial area with high traffic density
Shopping center C	Air conditioner	Commercial area with high traffic density
Supermarket A	Air conditioner	Residential area with moderate traffic density
Supermarket B	Air conditioner	Residential area with moderate traffic density
Furniture store	Natural	Residential area with moderate traffic density
Cinema A	Air conditioner	Commercial area with moderate traffic density
Cinema B	Air conditioner	Residential area with moderate traffic density
Cinema C	Air conditioner	Residential area with moderate traffic density
Railway station A	Natural	Urban area with moderate traffic density
Railway station B	Natural	Urban area with moderate traffic density
Inter-city bus station A	Natural	Urban area with moderate traffic density
Inter-city bus station B	Natural	Urban area with moderate traffic density
Inter-city bus station C	Natural	Urban area with moderate traffic density

was resealed and transported back to the laboratory immediately and stored in the refrigerator (below 4 °C) for analysis.

The absorbent was put into a tube with 10 mL of acetonitrile (ACN). Then the tube was sonicated for 15 min, and then 50 μL aliquots were injected into the HPLC (Agilent 1100, USA) fitted with UV detector and a Kromasil C18 reverse column (4.6 mm × 250 mm, 5 μm) using 60% ACN of water solution as the mobile phase at a flow rate of 1.0 mL/min. The UV wavelength was set at 360 nm.

2.4. Quality assurance and quality control

A regime of quality control was operated in the experiment. The instrument was calibrated using standard concentrations covering the concentration of interest. The concentrations and responses for all the carbonyls identified follows linear relationships ($R^2 > 0.99$). Cartridge laboratory blanks and cartridge field controls were analyzed to determine background levels of DNPH derivatives. Carbonyl levels in cartridge field controls were similar to those of the cartridge laboratory blanks. The average concentrations of cartridge blanks were within the acceptable range of EPA TO-11. Cartridge collection efficiency was determined with two cartridges in series, and over 90% of carbonyls were found in the first cartridge. Second elution tests indicated complete recovery of all the carbonyls. For a sample volume of 90 L, detection limits of DNPH derivatives for all the carbonyls were 0.15, 0.19, 0.09, 0.26, 0.26 and 0.42 $\mu g/m^3$ for formaldehyde, acetaldehyde, acetone, propionaldehyde, crotonaldehyde and butyraldehyde, respectively.

3. Results and discussion

3.1. Indoor carbonyl levels of different public places

Indoor air samples were collected in three shopping centers, two supermarkets, one furniture store, three inter-city bus stations, two railway stations and three cinemas from March to April, 2006. Table 2 showed the mass concentrations of measured carbonyl components inside public places. The mean concentration of total carbonyls was 146.5 $\mu g/m^3$ in indoor air. Formaldehyde was the most abundant carbonyls in most air samples, followed by acetone, acetaldehyde, crotonaldehyde, propionaldehyde and butyraldehyde with the average value of 90.6, 28.0, 18.4, 4.4, 3.3 and 1.9 $\mu g/m^3$, respectively. Formaldehyde and acetone accounted for 58.0 and 20.9% of the total carbonyls in indoor air, respectively. Equivalent concentrations of formaldehyde were also observed in indoor air of Mexico (11–97 $\mu g/m^3$) [5]. High levels of formaldehyde and acetone in indoor air were probably from the indoor materials and human activities. Related studies show that formaldehyde and acetone can be emitted by decorating- and refurbishing-materials [8]. Thus the presence of the indoor materials might result in the high levels of formaldehyde and acetone.

The carbonyl levels varied widely among public places. The furniture store presented the highest carbonyl concentration, followed by shopping centers, supermarkets and cinemas, while the carbonyl levels in the railway stations and inter-city bus stations were relatively lower.

Formaldehyde was found to be the largest contributor to carbonyls for the shopping centers, followed by acetone and acetaldehyde. The concentrations of propionaldehyde, crotonaldehyde and butyraldehyde in different shopping centers showed great differences among sites. In 2006, the total carbonyl concentration (301.1 $\mu g/m^3$) in indoor air of shopping center C was the highest since it has been newly painted and decorated. The carbonyl concentrations in shopping center A were similar to those in shopping center B with only a few exceptions. Compared with studies in France [13], the concentrations of formaldehyde and acetaldehyde obtained in the present study were much higher.

Indoor air measurements were conducted in the springs of 2006 and 2007, and the characteristics of sampling sites were recorded. Table 3 showed the carbonyl levels of shopping center A and C during two consecutive years. In the 2 years, shopping center A was refurbished in 2007, while shopping center C was refurbished in both of the years. In general, the formaldehyde concentrations in indoor air of shopping centers under refurbishment were higher than those under normal conditions. The refurbishment and decoration materials such as paint, drywall, adhesives, and so on, were reported to be important sources of formaldehyde [7,8]. Therefore, the high levels of carbonyls shortly after refurbishment might be due to the emissions of refurbishment and decoration materials.

Air samplings were conducted inside two supermarkets. The results showed that the mean acetaldehyde concentrations of supermarket A and B were comparatively higher: 29.6 and 56.4 $\mu g/m^3$, respectively. Other five carbonyls were relatively lower and varied between different supermarkets.

3.2. Indoor carbonyl levels of different areas in shopping centers and supermarkets

Carbonyl samples were collected in different areas of shopping centers in 2006, including cosmetic, men's garment, suit-dress, shoe, bedclothes, household appliance, children's thing, playroom and restaurant areas. Considering the toxicity and the pollution levels of the six determined carbonyls, formaldehyde and acetaldehyde were selected. Besides, taking account of other carbonyls, the total concentrations of six carbonyls were also compared. As was shown in Fig. 2, the total concentrations of carbonyls in the air of the bedclothes and restaurant areas were the highest in shopping

Table 2
Concentrations of carbonyl compounds in selected public places in 2006 (mean: μg/m^3)

Sampling sites	Formaldehyde	Acetaldehyde	Acetone	Propionaldehyde	Crotonaldehyde	Butyraldehyde	Total carbonyl compounds	*N*
Shopping center A								
Indoor	61.0	8.5	32.6	2.3	1.5	1.2	107.1	48
Outdoor	25.7	4.9	27.4	1.2	0.8	0.5	58.3	12
Shopping center B								
Indoor	67.7	9.5	38.0	2.5	5.1	1.6	124.4	52
Outdoor	15.6	5.0	22.6	1.4	0.7	Nd	45.7	12
Shopping center C								
Indoor	245.7	18.5	23.3	3.1	8.0	2.5	301.1	24
Outdoor	42.4	8.7	6.0	1.6	1.0	Nd	60.1	4
Supermarket A								
Indoor	52.7	29.6	16.3	4.6	6.7	1.9	111.7	27
Outdoor	12.7	9.7	7.3	1.9	0.8	Nd	32.7	4
Supermarket B								
Indoor	76.3	56.4	29.3	6.3	5.3	2.6	176.1	14
Outdoor	15.3	10.8	8.0	1.3	1.9	Nd	37.4	2
Furniture store								
Indoor	165.4	27.0	17.3	5.4	2.2	3.6	221.0	10
Outdoor	37.3	13.2	9.4	3.1	1.0	2.0	66.0	2
Cinema A								
Indoor	66.5	14.7	15.3	2.7	0.7	2.4	102.5	2
Cinema B								
Indoor	114.6	27.5	23.9	3.4	1.9	3.2	174.5	2
Cinema C								
Indoor	65.2	32.0	17.3	4.5	1.6	3.7	124.3	2
Railway station A								
Indoor	19.1	25.8	18.3	3.4	1.3	3.1	71.0	2
Railway station B								
Indoor	12.3	14.7	14.9	2.2	0.7	2.1	46.9	2
Inter-city bus station A								
Indoor	19.5	17.8	10.1	3.0	1.3	2.4	54.3	2
Inter-city bus station B								
Indoor	18.4	10.7	7.2	2.2	1.7	1.6	41.9	2
Inter-city bus station C								
Indoor	11.8	8.4	5.7	1.4	0.7	1.0	28.9	2
All samples								
Indoor	90.6	18.4	28.0	3.3	4.4	1.9	146.5	191
Outdoor	22.2	6.4	18.4	1.5	0.8	0.5	49.8	36

Mean: Arithmetic mean in sampling sites, *N*: number of samples, Nd: not detected.

centers, with the mean concentrations of 143.4 and 144.4 μg/m^3, respectively. This might suggested that the indoor carbonyl sources, such as bedclothes and cooking [6], account for the high indoor levels of carbonyls.

In addition, indoor air samples in different areas of supermarkets were measured. The sampling sites included the areas of bedclothes, shoe, cooked food, food, scour, undergarment, stationary and household appliance. The carbonyl concentrations in different areas were showed in Fig. 3. Among the different areas, the cooked food area presented the highest levels of the total carbonyls and acetaldehyde with the average values of 286.2 and 167.5 μg/m^3, respectively. Following the cooked food area, the stationary area exhibited comparatively higher carbonyl levels (Fig. 3). The stuffs in the supermarket were cooking food during all the working time in the cooked food area to supply the customers with the cooked food. As formaldehyde and acetaldehyde could be generated during cooking [6], the anthropogenic source, such as cooking, might explain the high carbonyl levels in cooked food area in supermarkets. Whereas high concentrations of carbonyls in stationary area were probably due to the emission from the notebooks and exercise books, since paper can emit a mass of formaldehyde [17]. The pollution levels of total carbonyls in the air of the other areas in supermarkets were almost the same. The different concentrations in the supermarkets and shopping centers might be due to the dif-

Table 3
Indoor carbonyl levels of different shopping centers (mean: μg/m^3)

	Year	Site Description	Formaldehyde	Acetaldehyde	Acetone	Butyraldehyde
Shopping center A	2006	Normal	61.0 ± 28.7	8.5 ± 4.9	32.6 ± 41.3	1.2 ± 1.5
	2007	Under refurbishment	114.4 ± 20.9	7.1 ± 0.6	23.3 ± 2.6	3.8 ± 4.2
Shopping center C	2006	Under refurbishment	245.7 ± 116.4	18.5 ± 4.8	23.3 ± 14.4	2.5 ± 2.0
	2007	Under refurbishment	196.8 ± 69.1	12.9 ± 1.6	38.4 ± 4.6	3.9 ± 0.7

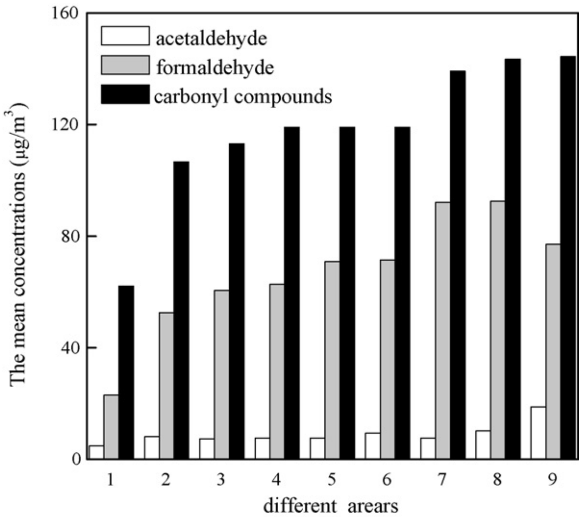

Fig. 2. Comparison of mean concentrations of formaldehyde, acetaldehyde and total carbonyl compounds in the air of different areas in shopping centers in 2006 (1–9: cosmetic, suit-dress, men's garment, shoe, children's thing, playroom, household appliance, bedclothes and restaurant areas).

ference of the raw materials of the bedclothes. The bedclothes sold in the shopping centers were made of leather or cotton. While the bedclothes sold in the supermarkets were mainly made of cotton or bamboo.

3.3. Outdoor carbonyl levels of public places

The carbonyl concentrations in outdoor air were determined for the selected public places and the corresponding data were also listed in Table 2. Among the carbonyls monitored in outdoor air, formaldehyde, acetone and acetaldehyde were the dominating pollutants, with the mean concentrations of 22.2, 18.4 and 6.4 $\mu g/m^3$, respectively, followed by propionaldehyde, crotonaldehyde and butyraldehyde. The total concentrations of carbonyls had an arithmetic mean value of 49.8 $\mu g/m^3$ in outdoor air, in which formaldehyde accounted for 43.2%, acetone accounted for 33.2% and acetaldehyde accounted for 15.1%. The mean levels for formaldehyde measured in Hangzhou were higher than those reported in other studies (Table 4). The mean level for acetaldehyde (6.4 $\mu g/m^3$) was in good agreement with that reported by Báez et al. [5], but higher than those measured by Cavalcante et al. [12], Viskari et al. [18] and Ho et al. [19].

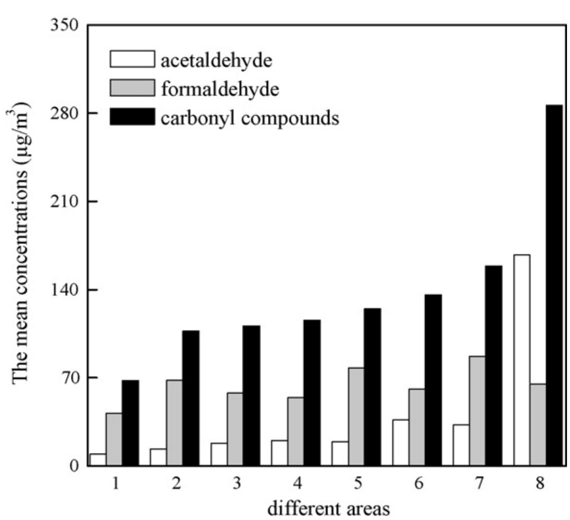

Fig. 3. Comparison of mean concentrations of formaldehyde, acetaldehyde and total carbonyl compounds in the air of different areas in supermarkets in 2006 (1–8: bedclothes, undergarment, shoe, scour, household appliance, food, stationary and cooked food areas).

Table 4
Comparison of outdoor formaldehyde and acetaldehyde levels with other studies (mean: $\mu g/m^3$)

Location	Formaldehyde	Acetaldehyde	References
Guangzhou, China	6.43–29.0	3.12–17.3	Feng et al. [9]
HongKong, China	4.13–5.27	1.73–2.53	Ho et al. [19]
Kuopio, Finland	1.3–2.8	1.1–3.2	Viskari et al. [18]
Xalapa City, Mexico	4.4	6	Báez et al. [5]
Fortaleza, Brazil	2.8	0.7	Cavalcante et al. [12]
Hangzhou, China	22.2	6.37	This study

3.4. I/O ratios analysis and indoor source implications

By comparison of the indoor and outdoor carbonyl concentrations, it was found that the ratios of I/O for each carbonyls were greater than 1 (Table 5). The I/O ratios in shopping center C were higher than that in other five places except for two or three carbonyls (e.g. acetaldehyde), and the I/O ratios for almost all components in Shopping center A were the lowest. The I/O ratio of acetaldehyde was especially high in Supermarket A and B. The difference in the I/O ratios might be due to the different ventilation conditions and indoor source strengths. Meanwhile, the most likely explanation to the ratios close to 1.0 was the preferential infiltration of the outdoor air. In addition, the I/O ratios of different components of carbonyls varied widely.

It was known that various elements inside a building were sources of carbonyls, such as decoration, furniture and consumer product [20–23]. The indoor ozone chemistry could play a role in generating indoor aldehydes, which were generated by the reaction of ozone with VOCs, especially with the presence of carpet [24]. The high carbonyl concentrations (221.0 $\mu g/m^3$) and I/O ratios in furniture store suggested that the important indoor sources might be indoor materials, especially the furniture. And it should be pointed out that most I/O ratios in shopping center C were the highest with only a few exceptions (Table 5), which could be explained by the usage of new decorating and refurbishing materials and the lack of the independent ventilation system. The comparatively higher concentrations and I/O ratios of carbonyls in the shopping centers and supermarkets were probably caused by the emission of the decorations and the consumer products. The special decorations and materials applied in the cinema could emit enhanced concentrations of carbonyls. The indoor concentrations of carbonyls in the stations were the lowest, which might explained by preferential ventilation.

3.5. Exposure and risk

The exposure (E_i) for an individual (i) due to intake processes (inhalation and ingestion) can be calculated from the equation of the US EPA [25]:

$$E_i = C_j \mathrm{IR}_i t_{ij} \quad (1)$$

where C is the concentration of the chemicals ($\mu g/m^3$), IR is the inhalation rate (m^3/h), t is the exposure time (h/d), and j is the microenvironment.

Indoor inhalation rates were estimated for an average person (IR = 0.63 m^3/h) according to EPA exposure factors [26]. Exposure (E) was calculated at different public places. The exposure time (t) in each environment was based upon the official working time

Table 5
The mean indoor/outdoor (I/O) ratios of carbonyl concentrations in 2006

Location	Formaldehyde	Acetaldehyde	Acetone	Propionaldehyde	Crotonaldehyde	Butyraldehyde
Shopping center A	3.3	2.0	1.5	2.7	3.4	3.6
Shopping center B	5.5	2.1	2.6	2.0	10.2	4.5
Shopping center C	6.1	2.2	3.3	2.4	10.2	8.1
Supermarket A	4.3	3.6	2.3	2.6	6.6	2.2
Supermarket B	5.0	5.7	3.7	4.8	2.8	–
Furniture store	4.4	1.9	1.8	1.7	2.4	2.0

and the average residence time for staffs, customers or passengers. For staffs, 8 h was considered. For passengers in the waiting rooms in bus stations and railway stations, a mean time of 1 h was considered. As for customers in other public places studied, a mean residence time of 2 h was considered. The exposure time used in the exposure assessment was based on the investigation of the custom of Chinese persons.

The mean and the highest exposures (95 percentile) for formaldehyde and acetaldehyde at different public places were estimated and compared with reported data of other places [5,9]. A mean residence time of 8 h (official working time) was considered for offices as exposure time (t) in Mexico City [4], while 6 h (the time of opening) was used in Guangzhou [9]. The results were shown in Tables 6 and 7. In the present study, the mean occupational exposure for formaldehyde in furniture store was the highest, followed by shopping centers and supermarkets. Meanwhile, supermarkets presented the highest occupational exposure for acetaldehyde, followed by furniture store and railway stations. Similar behaviors were observed for exposure for the customers and passenger. The occupational exposure for formaldehyde at shopping centers, furniture store and supermarkets in Hangzhou was much higher than that in the offices of Mexico City and that in ballrooms of Guangzhou [5,9]. Meanwhile, the occupational exposure for acetaldehyde in supermarkets, furniture store and railway stations were lower than those in ballrooms [9], although higher than those in offices [5]. The exposure for customers was lower than the occupational exposure of the staffs (Table 7).

The inhalation unit risk estimate of formaldehyde is $1.3 \times 10^{-5}\,(\mu g/m^3)^{-1}$ [27]. Acetaldehyde has been classified as B2, probable human carcinogen of low carcinogenic hazard, with an inhalation unit risk estimate of $2.2 \times 10^{-6}\,(\mu g/m^3)^{-1}$ [28]. Cancer risks for formaldehyde and acetaldehyde were calculated by using the inhalation unit risk, the mean concentrations and the highest (95 percentile) concentrations. Compared with other studies, the risks of formaldehyde in this study, except for the stations, were higher than the risks in ballrooms in Guangzhou, China [7] and even higher than the risks in offices in Mexico City [5], which was known as one of the most polluted cities in the world. Meanwhile, the risks of acetaldehyde, except for the shopping centers and bus stations, were significantly lower than those in ballrooms, but slightly higher than those in offices [5,9]. The high health risks at the public places might increase the chance of developing cancer for the human beings.

Cancer risks for formaldehyde and acetaldehyde should be viewed as preliminary because parameters, such as the ventilation rate, the duration and type of physical activity, were not determined

Table 6
Concentrations (C) and estimated exposure values (E) and health risks of carbonyl compounds in public air (for staffs) in 2006

Parameter	Formaldehyde						Acetaldehyde					
	C ($\mu g/m^3$)		E ($\mu g/d$)		Risk		C ($\mu g/m^3$)		E ($\mu g/d$)		Risk	
	A.M.	95th p.	A.M.	95th p.	A.M.	95th p.	A.M.	95th p.	A.M.	95th p.	A.M.	95th p.
Shopping centers[a]	125	228	630	1.15×10^3	1.6×10^{-3}	3.0×10^{-3}	12.2	17.6	61.3	88.7	2.7×10^{-5}	3.9×10^{-5}
Supermarkets[a]	64.5	75.1	325	379	8.4×10^{-4}	9.8×10^{-4}	43.0	55.1	217	278	9.5×10^{-5}	1.2×10^{-4}
Railway stations[a]	15.7	18.7	79.2	94.4	2.0×10^{-4}	2.4×10^{-4}	20.2	25.3	102	127	4.5×10^{-5}	5.6×10^{-5}
Bus stations[a]	16.6	19.4	83.5	97.8	2.2×10^{-4}	2.5×10^{-4}	12.3	17.1	62.1	86.3	2.7×10^{-5}	3.8×10^{-5}
Furniture store[a]	165	214	832	1.08×10^3	2.2×10^{-3}	2.8×10^{-3}	27.0	102.6	136	519	5.9×10^{-5}	2.3×10^{-4}
Ballroom[b]	33.1	55.0	124	209	4.4×10^{-4}	7.2×10^{-4}	100	226	378	853	2.3×10^{-4}	5.1×10^{-4}
Office[c]	26.2	34.4	132	173	3.4×10^{-4}	4.5×10^{-4}	19.3	32.7	97	165	4.2×10^{-5}	7.2×10^{-5}

A.M.: arithmetic mean; 95th p.: 95th percentile. Exposure time (t): (a) for the public places in the present study, 8 h were considered; (b) 6 h (the time of opening) was used; (c) a mean residence time of 8 h (official working time) was considered for offices.

[a] Present study, 2006.
[b] Guangzhou.
[c] Xalapa, Mexico.

Table 7
Concentrations (C), and estimated exposure values (E) and health risks of carbonyl compounds in public air (for costumers and passengers) in 2006

Parameter	Formaldehyde						Acetaldehyde					
	C ($\mu g/m^3$)		E ($\mu g/d$)		Risk		C ($\mu g/m^3$)		E ($\mu g/d$)		Risk	
	A.M.	95th p.	A.M.	95th p.	A.M.	95th p.	A.M.	95th p.	A.M.	95th p.	A.M.	95th p.
Shopping centers	125	228	157	288	1.6×10^{-3}	3.0×10^{-3}	12.2	17.6	15.3	22.2	2.7×10^{-5}	3.9×10^{-5}
Supermarkets	64.5	75.1	81.3	94.7	8.4×10^{-4}	9.8×10^{-4}	43.0	55.1	54.2	69.4	9.5×10^{-5}	1.2×10^{-4}
Railway stations	15.7	18.7	9.9	11.8	2.0×10^{-4}	2.4×10^{-4}	20.2	25.3	12.7	15.9	4.5×10^{-5}	5.6×10^{-5}
Bus stations	16.6	19.4	10.4	12.2	2.2×10^{-4}	2.5×10^{-4}	12.3	17.1	7.8	10.8	2.7×10^{-5}	3.8×10^{-5}
Furniture store	165	214	208	270	2.2×10^{-3}	2.8×10^{-3}	27.0	102.6	34.0	129	5.9×10^{-5}	2.3×10^{-4}
Cinemas	33.1	55.0	103	159	4.4×10^{-4}	7.2×10^{-4}	100	226	31.2	46.8	2.3×10^{-4}	5.1×10^{-4}

A.M.: arithmetic mean; 95th p.: 95th percentile. Exposure time (t): for railway stations and bus stations, 1 h was considered. For other public places studied, 2 h were considered.

and the relevant information was insufficient. In shopping centers, furniture stores and supermarkets, the sites where people walk around to choose commodities, it could be anticipated that people would achieve more intensive activities than usual, resulting in higher inhalation rates and higher risks comparing with just calm stay at resident homes, offices, restaurants and cinemas. As a result, the cancer risks there would be higher than the calculated values.

4. Conclusions

The carbonyl concentrations in indoor air were investigated at the selected public places in Hangzhou, China. The carbonyl concentrations in indoor air ranged from 25.0 to 490.0 $\mu g/m^3$, in which formaldehyde was the most abundant carbonyl compound, ranging from 10.2 to 425.1 $\mu g/m^3$. The carbonyl concentrations showed great differences among public places. The furniture store presented the highest carbonyl concentration, followed by shopping centers, supermarkets, cinemas, while the carbonyl levels in indoor air of the railway stations and inter-city bus stations were lower. The restaurant and bedclothes areas exhibited the highest levels of total carbonyls in shopping centers. The total concentrations of carbonyls in cooked food area were the highest in supermarkets. The I/O ratios varied widely by pollutants. The high carbonyl concentrations in indoor air and the high I/O ratios suggested the presence of the indoor sources of carbonyls. Preliminary estimate of the exposure and risk indicated that the public and occupational health risks for formaldehyde at selected public places of Hangzhou were higher than other studies with only a few exceptions.

Acknowledgments

This work was supported by grants from NSFC-JST (20621140003) and the National High Technology Research and Development Program of China (No. 2007AA061402, 2007AA061403).

References

[1] M. Hauptmann, J.H. Lubin, P.A. Stewart, R.B. Hayes, A. Blair, Mortality from solid cancers among workers in formaldehyde industries, Am. J. Epidemiol. 159 (2004) 1117–1130.
[2] WHO, Air Quality Guidelines for Europe, Second ed., WHO Regional Publications, European Series, Copenhagen, Denmark, 2000.
[3] IARC, Overall Evaluation of Carcinogenicity to Humans, Formaldehyde [50-00-0], Monographs Series, International Agency for Research on Cancer, Lyon, France, vol. 88, 2006.
[4] J.F. Zhang, Q.C. He, P.J. Lioy, Characteristics of aldehydes: concentrations, sources, and exposures for indoor and outdoor residential microenvironments, Environ. Sci. Technol. 28 (1994) 146–152.
[5] A.P. Báez, H. Padilla, R. Garcia, M.D.C. 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.
[6] J.F. Zhang, K.R. Smith, Emissions of carbonyl compounds from various Cookstoves in China, Environ. Sci. Technol. 33 (1999) 2311–2320.
[7] P. Fjällström, B. Andersson, C. Nilsson, Drying of linseed oil paints: the effects of substrate on the emission of aldehydes, Indoor Air 13 (2003) 277–282.
[8] N.L. Gilbert, D. Gauvin, M. Guay, M.E. Héroux, G. Dupuis, M. Legris, C.C. Chan, R.N. Dietz, B. Lévesque, Housing characteristics and indoor concentrations of nitrogen dioxide and formaldehyde in Quebec City, Canada, Environ. Res. 102 (2006) 1–8.
[9] Y.L. Feng, S. Wen, X.M. Wang, G.Y. Sheng, Q.S. He, J.H. Tang, J.M. Fu, Indoor and outdoor carbonyl compounds in the hotel ballrooms in Guangzhou, China, Atmos. Environ. 38 (2004) 103–112.
[10] H.X. Lü, S. Wen, Y.L. Feng, X.M. Wang, X.H. Bi, G.Y. Sheng, J.M. Fu, Indoor and outdoor carbonyl compounds and BTEX in the hospitals of Guangzhou, China, Sci. Total Environ. 368 (2006) 574–584.
[11] T. Takigawa, T. Horike, Y. Ohashi, H. Kataoka, D.H. Wang, S. Kira, Were volatile organic compounds the inducing factors for subjective symptoms of employees working in newly constructed hospitals, Environ. Toxicol. 19 (2004) 280–290.
[12] R.M. Cavalcante, C.S. Campelo, M.J. Barbosa, E.R. Silveira, T.V. Carvalho, R.F. Nascimento, Determination of carbonyl compounds in air and cancer risk assessment in an academic institute in Fortaleza, Brazil, Atmos. Environ. 40 (2006) 5701–5711.
[13] C. Marchand, B. Bulliot, S.L. Calve, P. Mirabel, Aldehyde measurements in indoor environments in Strasbourg (France), Atmos. Environ. 40 (2006) 1336–1345.
[14] T. Ohura, T. Amagai, Y. Senga, M. Fusaya, Organic air pollutants inside and outside residences in Shimizu, Japan: levels, sources and risks, Sci. Total Environ. 366 (2006) 485–499.
[15] Occupational Safety and Health Administration (OSHA), Fact Sheets Highlighting Program: Formaldehyde (29 CFR-1910.1048) and Acetaldehyde (29 CFR-1910.1000), US Department of Labor, 2002.
[16] US Environment Protection Agency (US EPA), Compendium method TO-11A. Determination of formaldehyde in ambient air using adsorbent cartridge followed by high performance liquid chromatography (HPLC) [Active Sampling Methodology] [S], 1999.
[17] G. Fantuzzi, G. Aggazzotti, E. Righi, L. Cavazzuti, G. Predieri, A. Franceschelli, Indoor air quality in the university libraries of Modena (Italy), Sci. Total Environ. 193 (1996) 49–56.
[18] E. Viskari, M. Vartiainen, P. Pasanen, Seasonal and diurnal variation in formaldehyde and acetaldehyde concentrations along a highway in Eastern Finland, Atmos. Environ. 34 (2000) 917–923.
[19] K.F. Ho, S.C. Lee, P.K.K. Louie, S.C. Zou, Seasonal variation of carbonyl compound concentrations in urban area of Hong Kong, Atmos. Environ. 36 (2002) 1259–1265.
[20] D.R. Crump, D. Gardiner, Sources and concentrations of aldehydes and ketones in indoor environments in the UK, Environ. Int. 15 (1989) 455–462.
[21] T.J. Kelly, D.L. Smith, J. Satola, Emission rates of formaldehyde from materials and consumer products found in California homes, Environ. Sci. Technol. 33 (1999) 81–88.
[22] P. Carlier, H. Hannachi, G. Mouvier, The chemistry of carbonyl compounds in the atmosphere—a review, Atmos. Environ. 20 (1986) 2079–2099.
[23] M.M. Samfield, Indoor Air Quality Data base for Organic Compounds, United States Environmental Protection Agency, 1992, EPA-600-R-92-025.
[24] G.C. Morrison, W.W. Nazaroff, The rate of ozone uptake on carpets: experimental studies, Environ. Sci. Technol. 34 (2000) 4963–4968.
[25] Environmental Protection Agency (US EPA), Guidelines for Exposure Assessment, Office of Research Development, Office of Health and Environmental Assessment, Washington, DC, 1992, EPA 600Z-92y001.
[26] Environmental Protection Agency (US EPA), Exposure Factors Handbook, Office of Health and Environmental Assessment, Washington, DC, 1990, EPA 600y8-89y043.
[27] US Environmental Protection Agency (US EPA), Integrated risk information system (IRIS) on formaldehyde, On-line IRIS 1991, CASRN 50-00-0.
[28] US Environmental Protection Agency (US EPA), Integrated risk information system (IRIS) on acetaldehyde, On-line IRIS 1991, CASRN 75-07-0.