Ambient levels of carbonyl compounds and their sources in Guangzhou, China

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Abstract

Ambient levels of carbonyl compounds and their possible sources, vehicular exhaust and cooking exhaust, were studied at seven places in Guangzhou, including five districts (a residential area, an industrial area, a botanical garden, a downtown area and a semi-rural area), a bus station and a restaurant during the period of June–September 2003. Nineteen carbonyl compounds were identified in the ambient air, of which acetone was the most abundant carbonyl, followed by formaldehyde and acetaldehyde. Only little changes were found in carbonyl concentration levels in the five different districts because of their dispersion and mixture in the atmosphere in summer. The lower correlations between the carbonyls' concentrations might result from the mixture of carbonyls derived from different sources, including strong photochemical reactions at noon in summer. Formaldehyde and acetaldehyde were the main carbonyls in bus station, while straight-chain carbonyls were comparatively abundant in cooking exhaust. Besides vehicular exhaust, cooking might be another major source of carbonyl compounds in Guangzhou City, especially for high molecular weight carbonyls.
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Keywords: Carbonyl compounds; Vehicular exhaust; Cooking exhaust; Photochemical reactions; Ambient level

1. Introduction

Carbonyl compounds are ubiquitous components of the atmosphere, which play an important role in atmospheric chemistry and have adverse health effects on humans (Carlier et al., 1986). Carbonyls are important precursors of free radicals, ozone, and peroxyacyl nitrates (Atkinson, 1990; Tanner et al., 1988; Grosjean et al., 1993a, b, 1994, 1996a). Several carbonyls including formaldehyde, acetaldehyde, and acrolein also have received attention as eye irritants, toxic air contaminants, mutagens, and carcinogens (Shepson et al., 1986).

Atmospheric carbonyl compounds are produced directly from incomplete combustion of biomass and fossil fuels (Baugh et al., 1987; Zhang and Smith, 1999; Schauer et al., 2001) and formed as major reaction products in the atmospheric oxidation of many anthropogenic hydrocarbons and other volatile organic compounds (VOCs) (Carlier, 1986; Aschmann et al., 2001). Natural sources also contribute to atmospheric concentrations of several carbonyls through biogenic emissions of some plants (Ciccioli et al., 1993; Kesselmeier et al., 1997; Müller et al., 2002; Wildt et al., 2003; Villanueva

et al., 2004) and photochemical oxidation of naturally emitted hydrocarbon precursors, e.g. isoprene (Grosjean et al., 1993a).

Our study was motivated by several considerations. The studies about ambient carbonyls in urban air are relatively rare in Guangzhou (Tang, 2002; Feng et al., 2004). The impact on ambient levels of carbonyls from direct emissions (such as vehicular exhaust, cooking exhaust) has not been examined yet. More information is needed to assess, for example, the effect of carbonyls on air pollution and the contribution of carbonyls to photochemical reactions. Guangzhou is one of the largest cities in South China and known as its heavy traffic. In metropolitan areas, vehicular emissions are important and possibly, at times, the predominant contributors to carbonyls, hydrocarbons and aerosols (Grosjean, 1982; Miguel, 1991). In recent, much attention has been paid to vehicular emissions (Siegl et al., 1999; Kean et al., 2001; Grosjean et al., 2001). Formaldehyde is typically the most abundant carbonyl in vehicular exhaust, although acetaldehyde and acetone each can be of similar magnitude sometimes (Sigsby et al., 1987; Grosjean et al., 2001). In this paper, ambient levels of carbonyls have been measured at five districts in Guangzhou. Vehicular exhaust and another important source, cooking emissions in the restaurant, are also studied.

2. Experimental section

2.1. Field operations

Samples were collected in Guangzhou on 15 July–20 September 2003. Two source sites and five ambient locations were selected as sampling sites. The sketch map was shown in Fig. 1. Samples were collected between 11:00 a.m. and 13:00 p.m. every day on 4–7 consecutive days in each place.

(i) A bus station near the Guangzhou East Railway Station in Tianhe District (Fig. 1, S1), which corresponded to an area of ca. $17,300\,m^2$, with a roof, 8 exits and 8 carriage drives. The predominant traffic was gasoline-fueled heavy-duty buses and only a small proportion of diesel-fueled buses. The bus station could raise the rate of 4500 bus/ day. It was not only a parking place, the buses came and went frequently and there were many passengers waiting for the buses. Two hours sampling per day was performed each day at 7 consecutive days.

(ii) A restaurant in Panyu District (S2). The sampling was conducted just opposite to the chimney on the top of a ten floor restaurant 30 m high. Everyday two samples were collected during the cooking time (about 2 h sampling duration at noon and in the evening, respectively). In all, 12 samples were collected on six consecutive days .

(iii) A small downtown location in Baiyun District (S3). All kinds of vehicles (including heavy-duty diesel trucks) were permitted to pass by and traffic jams were frequent. Four samples were collected.

(iv) An industrial area near a petrochemical factory in Huangpu District (S4). The sampling site was on the top of a 2 floor building 5 m above the ground level. Five samples were collected.

(v) The South China Botanical Garden in Tianhe District (S5), which was one of the three largest

(b) S1: Bus station; S2: Restaurant; S3: Downtown area;
S4: Industrial area; S5: Botanical garden;
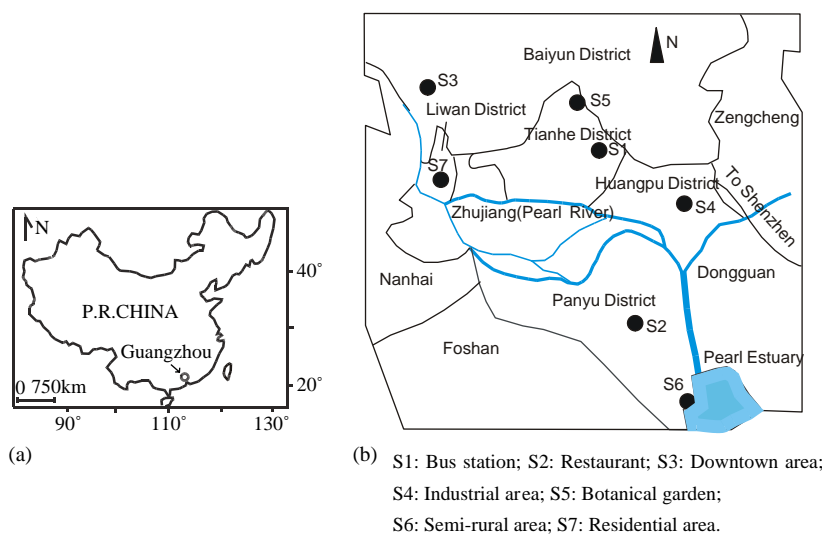S6: Semi-rural area; S7: Residential area.

Fig. 1. The sketch map of sampling sites. (a) The location of Guangzhou in China. (b) The sampling sites in Guangzhou. S1: Bus station; S2: Restaurant; S3: Downtown area; S4: Industrial area; S5: Botanical garden; S6: Semi-rural area; S7: Residential area.

gardens in China, with an area of ca. 3 million m^2. There was a highway in front of the botanical garden. It became a perfect place for people at leisure in summer. Nine samples were collected in all.

(vi) A semi-rural area along the Pearl River in the suburban of Panyu District (S6), about 160 km away from Guangzhou city and 4 km away from the nearest town. Six samples were collected.

(vii) A residential area in Liw an District of Guangzhou (S7), where there were high density of population and heavy traffic. There were hospitals, restaurants, and commercial streets. The sampling was conducted on the top of a ten-floor building. Five samples were collected.

2.2. Reagents

All solvents employed were HPLC grade. Water was double distilled and filtered by Milli-Q. The 2,4-dinitrophenylhydrazine (DNPH) was purchased from Fluka (USA) and further purified by recrystallizing two times in acetonitrile (Merck, Germany). The calibration standards (ChemService, USA) contained carbonyl-DNPH derivatives, including Mix 1 (DNPH derivatives of formaldehyde, acetaldehyde, acetone, acrolein, butyraldehyde, propionaldehyde, crotonaldehyde, benzaldehyde, 2,5-dimethylbenzaldehyde, hexaldehyde, isovaleraldehyde, valeraldehyde, *o*-tolualdehyde, *m*-tolualdehyde, *p*-tolualdehyde), Mix 2 (DNPH derivatives of formaldehyde, acetaldehyde, crotonaldehyde, propionaldehyde, butyraldehyde, cyclohexanone, valeraldehyde, hexaldehyde, heptaldehyde, octylaldehyde, nonanaldehyde, decylaldehyde) and 2-butanone-DNPH derivative.

2.3. Carbonyl sampling and analysis

The method had been used to collect carbonyl compounds in indoor and outdoor environments recently (Feng et al., 2004). In order to avoid the interference of the laboratory air, all the laboratory works were operated in a vacuum glove box (ZKX2, $800 \times 600 \times 700$ mm, Nanjing University Instrument Plant, China). Before each laboratory work, the glove box was vacuumized by a vacuum pump, and then filled with N_2 gas. The sampling medium was a Sep-Pak Silica Gel Cartridge (Waters, Millipore Corp). Each cartridge was rinsed by 10 ml of ACN slowly and then coated by passing 7 ml of the freshly made coating solution, which contained 60 ml DNPH-ACN-saturated solution and 2 ml concentrated *o*-phosphoric acid in 500 ml CAN, through the cartridge by gravity. When there was no more solution flowing out of the cartridge, the cartridge was dried with a gentle flow of nitrogen for 15 min. Then

the coated cartridges were wrapped in aluminum foils, sealed in hermetic Teflon bags, and stored in refrigerator at 4 °C until use. Three blank cartridges from each cartridge batch were analyzed and the results were all below the EPA blank criteria.

Samples were collected by drawing the air with a sampling pump (Thomas, USA) through the cartridge. A potassium iodide (KI) denuder was connected to the upstream of the cartridge to prevent the interference of ozone (Sirju and Shepson, 1995). The samples were collected for 2–3 h each day at a flow rate of 0.8–1.2 l min^{-1}. The flow rate was measured with a digital flow meter (DryCal DC Lite, Bios Corp., USA) during sampling. After sampling, each cartridge was wrapped in aluminum foil, resealed with a Teflon bag, and transported back to the laboratory and stored in the refrigerator before being analyzed. Each sampling program included one laboratory blank and one field blank. At each sampling site, two field samples were collected with back-up cartridge to evaluate breakthrough.

The sampled cartridges were eluted slowly with 2 ml of ACN into a 2-ml volumetric flask, stored in refrigerated conditions until use. The eluted samples were stable at 4 °C for up to one month. A 10-µl aliquot was injected into the HPLC system through an autosampler. The HPLC system was HP1100. The analytical conditions were as follows: Agilent SB—C18 reverse column (250×4.6 mm, 5 µm); gradient mobile phase: 60–70% ACN of water solution for 20 min, 70–100% ACN for 3 min, 100% ACN for 4 min, 100–60% ACN for 1 min, and then 60% ACN for 5 min; mobile-phase flow rate: 1 ml min^{-1}; detector: UV at 360 nm.

2.4. Quality assurance and quality control

The solvents used were of the HPLC grade and tested for purities by HPLC when a new lot number was used. One laboratory blank and one field blank were analyzed each day during sampling. In each place, two field samples were collocated with back-up cartridge to evaluate breakthrough. Identification and quantification of carbonyl compounds were based on their retention times and peak areas, respectively. The instrument was calibrated using five standard concentrations (from 0.5 to 10 µg ml^{-1}) covering the concentration of interest for each work. There were very good linear relationships ($R^2 > 0.999$) between the concentrations and responses for all carbonyls identified. Calibration standard run daily to ensure the instruments being stabilized. Cartridge collection efficiency was determined with two cartridges in series, and over 99% of carbonyl compounds were found in the first cartridge. Second elution tests indicated complete recovery of all of the carbonyls. Relative percent differences (RPDs) for duplicate

analysis were less than 5%. Method detection limits (MDLs) were determined by using seven replicate analyses of the working standards at the lowest concentration. The MDLs of present study were found to range from 0.05 to 0.15 μg m^{-3} for various carbonyls of 1201 sampling volume.

3. Results and discussion

3.1. Carbonyls identified and their concentrations in the ambient air

Twenty-one carbonyl compounds were measured in the ambient air, including formaldehyde, acetaldehyde, acrolein, acetone, propionaldehyde, crotonaldehyde, 2-butanone, butyraldehyde, benzaldehyde, isovaleraldehyde, cyclohexanone, valeraldehyde, p-tolualdehyde, m/o-tolualdehyde, hexaldehyde, 2,5-dimethylbenzaldehyde, heptaldehyde, octylaldehyde, nonanaldehyde and decylaldehyde (the sum of m-tolualdehyde and o-tolualdehyde was reported because they could not be separated by the analytical method). Arithmetic mean concentrations of carbonyl compounds were listed in Table 1. Acrolein was not detected in all the ambient air samples, p-tolualdehyde only presented in one sample and 2, 5 -dimethylbenzaldehyde was detected in 8 samples.

Of the 21 carbonyls listed in Table 1, acetone was the most abundant carbonyl in many samples and accounted for 24–39% of the total ambient carbonyl concentrations (Fig. 2). Ambient levels of acetone ranged from 7.20 to 30.32 μg m^{-3} (average 17.76 μg m^{-3}) (Fig. 3 and Table 1); the concentrations were higher (22.10–29.42 μg m^{-3}) at the downtown location and lower at the semi-rural area (7.2–17.60 μg m^{-3}) (Fig. 3). The mean concentrations of acetone in the industrial area (22.06 μg m^{-3}) were also a little higher, which possibly was because the industrial area was near a large petrochemical plant. Formaldehyde concentrations ranged from 6.38 to 16.42 μg m^{-3} and from 8.64 to 24.09 μg m^{-3} in the semi rural area (average 12.02 μg m^{-3}) and in the botanical garden (average 15.20 μg m^{-3}), respectively. Acetaldehyde concentrations were 3.96–12.66 μg m^{-3} and higher at the residential (10.87 μg m^{-3}) and downtown area (9.51 μg m^{-3}). The three carbonyls, formaldehyde, acetaldehyde and acetone, which had been monitored in many urban areas in other countries, accounted for 62–71% of the total ambient carbonyl concentrations (Fig. 2).

One reason for the high acetone concentrations in the ambient air was that the lifetimes of acetone for removal by photolysis and OH reaction were approximately 40 and 20 days in the atmosphere, respectively. In contrast, the lifetimes of formaldehyde and acetaldehyde for

reaction with OH were roughly $1\frac{1}{2}$ h to 1 day (Shepson et al., 1991; Atkinson, 2000). It thus seemed reasonable to expect that acetone concentrations should be higher (Shepson et al., 1991). Another reason was that acetone might be used as industrial solvent in many paint manufacturing and other industries located around Guangzhou city. Cetin et al. (2003) also found that the concentrations of acetone around the petrochemical refinery (23.4 $\pm$ 30.2 μg m^{-3}) were 2–3 times higher than those measured at suburban site (9.1 $\pm$ 6.1 μg m^{-3}).

Propionaldehyde, 2-butanone, butyraldehyde, cyclohexanone and benzaldehyde were relatively abundant and each compound accounted for 1–12% of the total carbonyl concentrations (Fig. 2). The sum of the 6 kinds of carbonyls (acrolein, crotonaldehyde, isovaleraldehyde, p-tolualdehyde, m/o-tolualdehyde and 2,5-dimethylbenzaldehyde) accounted for 2–5% of the total carbonyls, and the 6 straight-chain carbonyls (C$_5$–C$_{10}$) together accounted for 7–14% (Fig. 2). The most abundant high molecular weight carbonyl was nonanaldehyde (average concentrations ranged from 1.72 to 2.90 μg m^{-3}), which was consistent with the result of other studies (Grosjean et al., 2002). In natural environments, nonanaldehyde was also found to be one of the most abundant components at the site where Mediterranean vegetation was growing (Ciccioli et al., 1993). Yokouchi et al. (1990) found that semi-volatile aldehydes (C$_5$–C$_{11}$) were present ubiquitously, of which nonanaldehyde was always the most abundant one in two remote islands and in an inland local city. These aldehydes were considered to be naturally derived. The percentage of C$_5$–C$_{10}$ carbonyls of the whole carbonyls was higher (14%) in the Botanical Garden (Fig. 4), part of them might come from the vegetation emissions (Wildt et al., 2003). In the cooking exhaust, nonanaldehyde was also abundant, and this would be discussed later.

The total carbonyl concentration was the lowest in the semi-rural area (49.31 μg m^{-3}), and higher in the residential area (67.89 μg m^{-3}) and downtown area (66.15 μg m^{-3}). The concentrations of carbonyls in the semi-rural area studied were only slightly lower than those of other sites in Guangzhou and much higher than that of other semi-rural areas abroad (Christensen et al., 2000 and references therein). The semi-rural area in our study was far away from the nearest town, because of locating in the downwind of a coal-fired power station, which might be affected by the pollutants from there. Liwan District was the old residential area of Guangzhou, where there were high density of population, hospitals, commercial streets, restaurants and also busy traffic. The carbonyl concentrations in the downtown area were very high due to the traffic of heavy-duty diesel trucks. Previous studies indicated that carbonyls were major components of diesel exhaust emissions

Table 1
Concentrations of carbonyl compounds in the sampling sites ($\mu g\,m^{-3}$)

Compounds	Botanical garden Arith.mean ± SD	Residential area Arith.mean ± SD	Downtown area Arith.mean ± SD	Semi:rural area Arith.mean ± SD	Industrial area Arith.mean ± SD	Bus station Arith.mean ± SD	Restaurant Arith.mean ± SD
Formaldehyde	15.20 ± 5.70	13.83 ± 2.21	12.09 ± 1.78	12.02 ± 3.48	14.07 ± 3.11	66.97 ± 14.90	66.90 ± 20
Acetaldehyde	7.66 ± 1.64	10.87 ± 1.64	9.51 ± 3.38	7.24 ± 2.12	7.38 ± 2.12	23.15 ± 3.38	85.18 ± 19.39
Acrolein	Nd	Nd	Nd	Nd	Nd	1.48 ± 0.54	Nd
Acetone	15.53 ± 3.61	17.75 ± 6.33	25.98 ± 3.84	12.05 ± 3.99	22.06 ± 5.79	15.61 ± 8.10	52.63 ± 21.39
Propionaldehyde	1.56 ± 0.57	2.74 ± 0.46	1.94 ± 0.80	2.00 ± 0.80	1.35 ± 0.29	4.05 ± 1.09	11.94 ± 5.30
Crotonaldehyde	0.21 ± 0.05	Nd	Nd	0.15 ± 0.06	0.41 ± 0.08	1.27 ± 0.24	3.16 ± 1.02
2-Butanone	2.95 ± 0.75	8.54 ± 3.62	5.57 ± 1.72	5.19 ± 2.05	4.61 ± 1.73	3.90 ± 0.90	8.97 ± 2.30
Butyraldehyde	1.30 ± 0.45	2.02 ± 0.45	1.42 ± 0.40	1.48 ± 0.61	0.88 ± 0.22	3.94 ± 1.73	12.12 ± 3.72
Benzaldehyde	0.89 ± 0.20	1.99 ± 0.19	1.18 ± 0.30	1.84 ± 0.86	0.73 ± 0.28	1.73 ± 0.30	1.90 ± 0.96
Isovaleraldehyde	0.89 ± 0.44	0.84 ± 0.18	0.62 ± 0.15	0.34 ± 0.16	0.29 ± 0.32	0.61 ± 0.29	1.13 ± 0.35
Cyclohexanone	0.67 ± 0.34	2.67 ± 1.02	1.92 ± 1.68	2.53 ± 1.42	1.28 ± 0.38	0.96 ± 0.51	5.45 ± 1.39
Valeraldehyde	0.77 ± 0.23	0.91 ± 0.12	0.64 ± 0.11	0.63 ± 0.16	2.26 ± 0.63	1.39 ± 0.45	17.52 ± 5.28
p-Tolualdehyde	Nd	Nd	Nd	Nd	0.52[b]	0.72 ± 0.21	0.93 ± 0.26
m/o-Tolualdehyde	0.63 ± 0.21	0.76 ± 0.29	0.98 ± 0.46	0.46 ± 0.24	1.79 ± 0.30	1.74 ± 0.96	1.32 ± 0.59
Hexaldehyde	0.94 ± 0.49	1.26 ± 0.23	1.19 ± 0.10	0.55 ± 0.08	1.21 ± 0.11	1.15 ± 0.18	28.36 ± 7.92
2,5-dimethylbenzaldehyde	0.40 ± 0.08[a]	Nd	0.45 ± 0.16[a]	Nd	Nd	0.74 ± 0.42	1.31[b]
Heptaldehyde	0.51 ± 0.12	0.36 ± 0.19	0.35 ± 0.04	0.30 ± 0.02	0.55 ± 0.14	0.73 ± 0.13	9.35 ± 2.35
Octylaldehyde	1.53 ± 1.25	0.42 ± 0.12	0.28 ± 0.04	0.35 ± 0.08	0.79 ± 0.48	1.82 ± 0.74	11.54 ± 2.57
Nonanaldehyde	3.08 ± 1.11	2.55 ± 0.66	2.02 ± 0.55	1.74 ± 0.33	2.25 ± 1.01	1.89 ± 0.46	30.93 ± 6.35
Decylaldehyde	0.82 ± 0.15	0.38 ± 0.05	0.46 ± 0.18	0.44 ± 0.12	0.29 ± 0.33	0.65 ± 0.24	3.41 ± 0.71
Total	52.66 ± 8.22	67.49 ± 11.90	66.06 ± 9.20	49.31 ± 15.58	62.24 ± 11.43	134.05 ± 20.58	354.03 ± 85.39

Arith.mean: Arithmetic mean. SD: Standard deviation. Nd: Not detected.
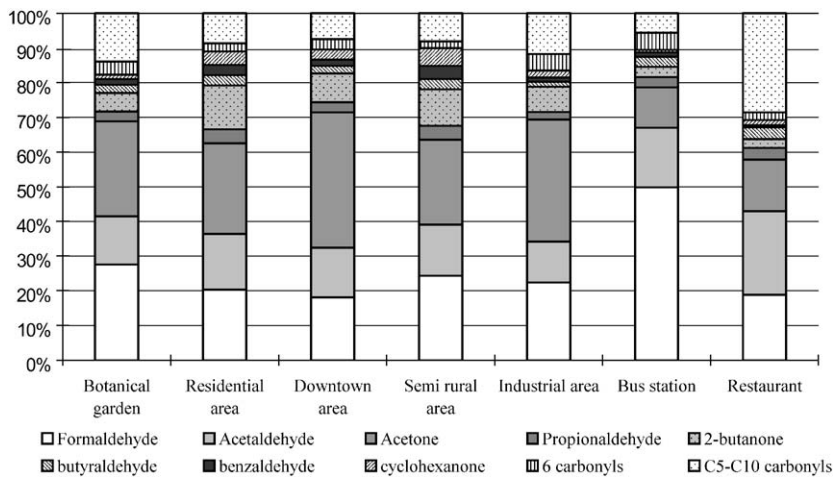
[a]Four samples average.

[b]Only one sample.

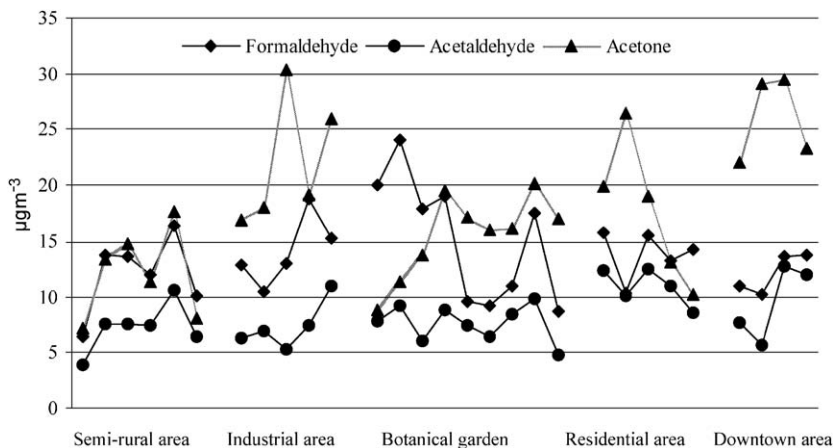Fig. 2. The percentage of carbonyl compounds in five sampling sites.

Fig. 3. The ambient concentrations ($\mu g\,m^{-3}$) of formaldehyde, acetaldehyde and acetone in five different locations.

(Siegl et al., 1999; Schauer et al., 1999a). However, the differences of the total carbonyls' concentrations were small among the five sites studied (10–20%). Carbonyl compounds were volatile and can easily mix or disperse in the atmosphere in summer. Tang (2002) found that the concentrations of carbonyls had little changes both at the ground and at the top of a ten-floor building (50 m) along a highway in Guangzhou, resulting from rapid mixing of air in vertical dimension. This might be the main reason that the carbonyl levels were little change in the different urban area of Guangzhou in summer (Table 2).

The comparisons between this study and previous studies in Guangzhou, Hong Kong and other studies of

most polluted cities in the world were listed in Table 2. In this study, the concentrations of carbonyls were much higher than that in Hong Kong (Ho et al., 2002). Average concentrations of formaldehyde, acetaldehyde and acetone were 13.68, 8.33 and 17.76 $\mu g\,m^{-3}$, respectively, in Guangzhou, compared to the data of 5.27, 2.53 and 1.14 $\mu g\,m^{-3}$ at TW station of Hong Kong, where there were higher concentrations of carbonyls relative to the other two stations. Concentrations of acetaldehyde were lower comparing to Brazil, where ethanol was used as vehicle fuel (Grosjean et al., 2002). Most of the carbonyl concentrations in Guangzhou were lower than that in the suburban of New Jersey (Zhang et al., 1994) and Rome (Possanzini et al.,
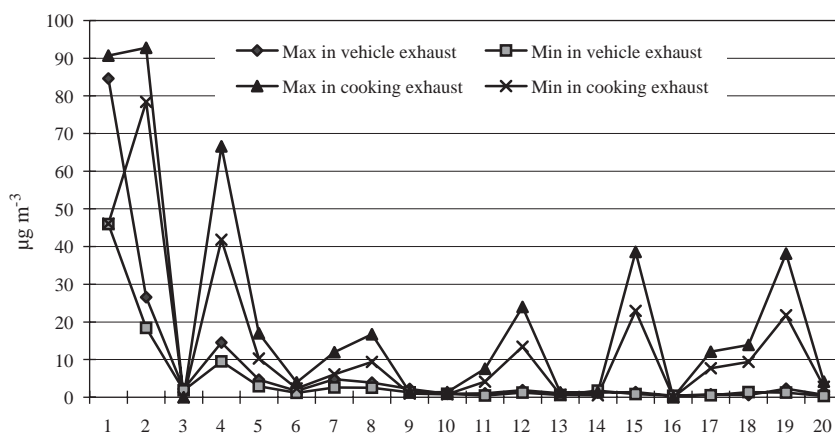
Fig. 4. The max and min concentrations ($\mu g\,m^{-3}$) of carbonyl compounds in the vehicle exhaust and cooking exhaust from the restaurant. (1) Formaldehyde; (2) acetaldehyde; (3) acrolein; (4) acetone; (5) propionaldehyde; (6) crotonaldehyde; (7) 2-butanone; (8) butyraldehyde; (9) benzaldehyde; (10) isovaleraldehyde; (11) cyclohexanone; (12) valeraldehyde; (13) *p*-tolualdehyde; (14) *m/o*-tolualdehyde; (15) hexaldehyde; (16) 2,5-dimethylbenzaldehyde; (17) heptaldehyde; (18) octylaldehyde; (19) nonanaldehyde; (20) decylaldehyde.

Table 2
Comparison of mean concentrations of carbonyl compounds with other studies ($\mu g\,m^{-3}$)

Locations	Guangzhou China[a]	Guangzhou China[b]	Guangzhou China[c]	Rio de Janeiro Brazil[d]	Los Angeles USA[e]	Rome Italy[f]	New Jersey United states[g]	HKPU Hong Kong	TW China[h]	CW
Formaldehyde	13.68	14.5	13.88	10.84	7.66	17.0	15.37	4.13	5.27	4.53
Acetaldehyde	8.33	8.9	7.92	10.43	6.84	9.3	4.75	2.01	2.53	1.73
Acetone	17.76	14.1	—	4.14	1.24	6.8	—	1.43	1.14	1.34
Propionaldehyde	1.87	1.7	1.47	1.05	1.66	1.8	3.01	0.24	0.48	0.26
Crotonaldehyde	0.15	0.3	0.41	0.30	0.72	—	—	—	—	—
2-Butanone	5.02	3.5	7.18	1.42	1.73	—	—	0.42	1.19	0.34
Butyraldehyde	1.41	1.3	1.01	0.48	1.95	—	1.47	0.15	0.23	0.16
Benzaldehyde	1.23	1.5	1.15	1.08	0	0.7	1.08	1.06	1.15	0.50
Isovaleraldehyde	0.59	1.2	0.44	0.27	—		1.30	—	—	—
Cyclohexanone	1.68	1.7	2.55	—	1.99		—	—	—	—
Valeraldehyde	1.01	1.2	0.43	0.27	0.92		2.81	0.24	0.25	0.16
m/o-Tolualdehyde	0.86	2.2	0.48	0.40	—		—	—	—	—
Hexaldehyde	0.99	0.6	0.83	0.27	1.53		—	0.89	0.37	0.23
Heptaldehyde	0.42	0.2	0.51	0.08	2.33		2.45	—	—	—
Octylaldehyde	0.75	0.2	0.28	0.10	—		—	—	—	—
Nonanaldehyde	2.42	1.4	2.06	2.09	—		—	—	—	—
decylaldehyde	0.47	0.5	0.4	1.47	—		—	—	—	—

[a]This study.
[b]Tang (2002).
[c]Feng et al. (2004).
[d]Grosjean et al., 2002.
[e]Grosjean et al. (1996b).
[f]Possanzini et al. (1996).
[g]Zhang et al. (1994).
[h]Ho et al. (2002).

1996). The highest mean concentrations in the outdoor environments in the literature of recent ten years were $43.5\,\mu g\,m^{-3}$ for formaldehyde and $33.8\,\mu g\,m^{-3}$ for acetaldehyde, in Mexico City (Baéz et

al., 1995). The higher acetone concentrations observed in the ambient air in present study were in accordance with previous studies (Shepson et al., 1991; Christensen et al., 2000).

3.2. Characteristics of carbonyl compounds from vehicular exhaust and cooking exhaust and their impacts on the ambient air

All the listed carbonyls in Table 1 were identified at the bus station. Nearly 80% of the carbonyls consisted of formaldehyde, acetaldehyde and acetone (Fig. 2). Formaldehyde $(66.97 \pm 14.90 \, \mu g \, m^{-3})$ was the most abundant carbonyl, accounting for 50.28% of the total carbonyls, followed by acetaldehyde $(23.15 \pm 3.18 \, \mu g \, m^{-3})$, accounting for 17.38%. The highest formaldehyde and acetaldehyde concentrations were $85.67 \, \mu g \, m^{-3}$ and $28.60 \, \mu g \, m^{-3}$, respectively (Fig. 4).

It was known that the carbonyls could be emitted from diesel vehicles (Sagebiel et al., 1996). Some components in fuel could produce more carbonyl compounds in combustion exhaust. For example, aromatic hydrocarbons were presented in gasoline, especially toluene and xylene, which were known to be precursors of benzaldehyde and tolualdehydes (Kaiser et al., 1991; Kean et al., 2001). On-road measurements and dynamometer test indicated that carbonyl compounds accounted for 30–60% of the gas-phase organic compounds emitted from diesel-fueled vehicles and 3–5% for gasoline-fueled vehicles (Kean et al., 2001; Siegl et al., 1999; Schauer et al., 1999a). For comparison, the percentages of each carbonyl among the 12 carbonyls were calculated and listed in Table 3. Formaldehyde and acetaldehyde accounted for 46–73% of the most abundant 12 carbonyls in these measurements. The percentage of formaldehyde plus acetaldehyde was 72.3% in this study, which was very close to the data of on-road measurement by Kean et al.

(72.7%). But the situation in the bus station was different from on-road emissions in regard to the compositions of gasoline and diesel or the types of vehicles. There were both gasoline and diesel-fueled vehicles in the bus station (gasoline vehicles accounted for about 90%). Carbonyl formation was most pronounced during engine start-up and off-cycle conditions, because under these partial oxidation conditions, more carbonyl compounds were produced (Baugh et al., 1987; Kean et al., 2001).

In cooking exhaust, acrolein and 2,5-dimethylbenzaldehyde were below our detection limits in all the samples. The straight-chain compounds (i.e. C_1, C_2, C_3, C_4, C_5, C_6) were relatively more abundant than the aromatic carbonyls (benzaldehyde, p-tolualdehyde and m/o-tolualdehyde) and the branch-chain carbonyls (isovaleraldehyde, and 2,5-dimethylbenzaldehyde). Both the present study and other studies all indicated that C_5–C_{10} aldehydes were relatively abundant in the cooking exhaust (Shimoda et al., 1997; Schauer et al., 2002). The most abundant carbonyl was acetaldehyde $(85.18 \pm 19.39 \, \mu g \, m^{-3})$, followed by formaldehyde $(66.90 \pm 20.00 \, \mu g \, m^{-3})$ and acetone $(52.63 \pm 21.39 \, \mu g \, m^{-3})$ (Table 1). Significant quantities of heavy aliphatic n-aldehydes were also found in the meat cooking exhaust (Schauer et al., 1999b). Nonanaldehyde concentration was as high as $30.93 \pm 6.35 \, \mu g \, m^{-3}$ in the cooking exhaust, which was likely formed from the decomposition of the unsaturated fatty acids (Schauer et al., 2002). The concentrations of valeraldehyde, butyraldehyde, propionaldehyde and octylaldehyde were also higher than $10 \, \mu g \, m^{-3}$. Most carbonyl compounds were formed from food and oil during cooking (Schulte,

Table 3

Comparison of the relative percentage of carbonyl compounds in vehicle exhaust with other studies

Species	Percent of the total carbonyls (%)			
	On-road[a]	On-road[b]	Dynamometer test[c]	Bus station[d]
Formaldehyde	42.2	57.8	16.0	53.7
Acetaldehyde	17.1	14.9	30.0	18.6
Acrolein	3.2	2.0	2.4	1.2
Acetone	16.7	7.5	15.8	12.5
Propionaldehyde	2.6	1.6	10.1	3.2
Crotonaldehyde	4.8	2.0	9.6	1.0
2-Butanone	3.6	1.0	5.4	3.1
Butyraldehyde	1.5	1.1	0.9	3.2
Benzaldehyde	3.4	9.1	2.7	1.4
Hexaldehyde	1.6	0.4	1.6	0.9
2,5-dimethylbenzaldehyde	2.6	2.2	2.9	0.6
heptaldehyde	0.8	0.2	2.3	0.6

[a] On-road emissions, 40%light and 60%heavy duty diesel vehicles, Grojean et al. (2001).
[b] On-road emissions, light-duty gasoline, Kean et al. (2001).
[c] Dynamometer test, medium duty diesel trucks, Schauer et al. (1999a, b).
[d] Bus station, heavy-duty 10%diesel+90%gasoline vehicles, Present study.

1964). Both the foods and the oils could produce carbonyl compounds during heat treatment (Reindl and Stan, 1982; Yasuhara and Shibamoto, 1995; Schauer et al., 2002). Rogge et al. (1991) observed that large amounts of semi-volatile aldehydes, especially nonanaldehyde, could be released during charbroiling and meat-cooking operations.

Fig. 4 gave the concentrations of carbonyl compounds in bus station and in cooking exhaust from restaurant. Although the mean concentrations of formaldehyde $(66.97 \, \mu g \, m^{-3}, 66.90 \, \mu g \, m^{-3}$, respectively) were close, the sum of the other carbonyls from the cooking exhaust were nearly five times higher than that at bus station, especially for high molecular weight aldehydes $(C_5–C_{10})$. Meat charbroiling was one of the few sources identified for the high molecular weight aldehydes measured in the urban atmosphere in USA (Schauer et al., 1999b). Guangzhou was popular for its rich and exotic dishes both at home and abroad. Scattered all over the city, there were over 5000 restaurants, teahouses and snack eateries. About 730 million cubic meters exhausts were emitted from the restaurants just in 2002 (B. Wang, private communication, 2004). It was reasonable to reckon that cooking exhaust from all kinds of restaurants should be one of the most important sources of carbonyls in the urban air.

3.3. The concentration ratios of carbonyl compounds

Formaldehyde/acetaldehyde (C_1/C_2) and acetaldehyde/propionaldehyde (C_2/C_3) ratios were also measured (Table 4). C_1/C_2 ratios usually varied from 1 to 2 (urban area) to about 10 (forest area); therefore they could be used as a measure of a biogenic source of formaldehyde (Shepson et al., 1991). C_2/C_3 ratios should be used likewise as indicators of anthropogenic origin for ambient carbonyls, since propionaldehyde was believed to be associated only with anthropogenic

emissions. C_2/C_3 would be high in rural atmospheres and low in polluted urban air. The ratios in this study and other studies were listed in Table 4. C_1/C_2 ratios all ranged from 1 to 2 at the five sampling sites. C_2/C_3 ratios were 3.79–5.42, similar to Rome (Possanzini et al., 1996), which might indicate the strong emissions from urban cities. But recent studies found that some plants could emit many kinds of carbonyls including formaldehyde, acetaldehyde and propionaldehyde (Villanueva et al., 2004; Martin et al., 1999), the ratios of C_1/C_2 were lower than 2 in rural and forest areas and higher than 2 in urban areas. Therefore, the concentration ratios of carbonyl compounds should be used carefully.

3.4. Correlations of carbonyl concentrations and their possible sources

The correlations between 14 carbonyls detected in all samples in the ambient air were shown in Table 5. Lower correlations of carbonyl concentration were found between most of the carbonyls, especially for formaldehyde and acetone, possibly resulting from the complex sources of the carbonyls. For example, formaldehyde had many sources except vehicular exhaust, e.g., produced by photooxidation of VOCs, especially in hot summer. Acetone had long lifetime in the atmosphere and could also be emitted from solvents used in the industry. $C_5–C_{10}$ carbonyls had lower correlations with other carbonyls, part of which might come from vegetation, because there were many kinds of trees at each sampling site. They might also derive from the cooking exhaust, in which there were large quantities of $C_5–C_{10}$ carbonyls. As discussed above, large percentages of $C_5–C_{10}$ carbonyls were found in the Botanical Garden and in the cooking exhaust (Fig. 2). There were excellent correlations ($R = 0.94$) between Propionaldehyde and butyraldehyde, and relatively good correlations ($R > 0.5$) between propionaldehyde, butyraldehyde, acetaldehyde,

Table 4
Comparison of C_1/C_2 and C_2/C_3 concentration ratios in Guangzhou and in other areas

Location	C_1/C_2	Range	C_2/C_3	Range	References
Semi-rural area	1.66	1.56–1.82	3.79	3.21–4.66	This study
Downtown area	1.36	1.07–1.82	5.05	4.71–5.94	This study
Residential area	1.28	1.03–1.67	3.98	3.84–4.39	This study
Botanical garden	2.00	1.28–2.93	5.12	4.05–7.07	This study
Industrial area	1.98	1.40–2.53	5.42	4.56–6.29	This study
Guangzhou,China(urban)	1.81	1.3–2.42	6.16	3.25–13.87	Feng et al. (2004)
Rome, Italy(urban)	2.1	0.8–4.1	5.2	3.1–8.7	Possanzini et al. (1996)
Mexico City (urban)	2.91	0.77–5.68			Baéz et al. (1995)
HongKong, China (urban)	2.1		8.38		Ho et al. (2002)
New Jersy ,USA(surburban)	5.8	1.1–22.0	2.3	0.8–10.4	Zhang et al. (1994)
Langmuir,Mexico(forested)	1.57		0.63		Villanueva et al. (2004)
Socorro,NM,Mexico(rural)	1.66		0.38		Villanueva et al. (2004)
Los Angeles, USA(urban)	0.91	0.44–2.13	3.84		Grosjean et al. (1996b)

Table 5
Correlations of carbonyl compounds in the ambient air at five locations of Guangzhou city

Compounds	1	2	3	4	5	6	7	8	9	10	11	12	13
Formaldehyde (1)													
Acetaldehyde (2)	0.33												
Acetone (3)	−0.31	0.18											
Propionaldehyde (4)	0.22	0.78[a]	0.67[a]										
2-butanone (5)	0.03	0.65[a]	0.33	0.66[a]									
Butyraldehyde (6)	0.15	0.68[a]	0.08	0.94[a]	0.61[a]								
Benzaldehyde (7)	0.07	0.52[a]	−0.04	0.69[a]	0.64[a]	0.69[a]							
Cyclohexanone (8)	−0.05	0.52[a]	0.20	0.63[a]	0.79[a]	0.57[a]	0.74[a]						
Valeraldehyde (9)	−0.03	−0.10	0.41	−0.21	−0.03	−0.35	−0.29	−0.13					
Hexataldehyde (10)	−0.16	−0.26	0.48	0.07	0.06	0.02	−0.24	−0.12	0.42				
Heptaldehyde (11)	−0.09	−0.04	0.24	−0.21	−0.28	−0.16	−0.32	−0.42	0.55a	0.38			
Octylaldehyde (12)	0.33	−0.05	−0.30	−0.14	−0.25	−0.10	−0.17	−0.33	0.00	−0.34	0.38		
Nonanaldehyde (13)	0.13	0.05	−0.16	−0.18	−0.22	−0.11	−0.18	−0.32	0.11	0.47	0.49[a]	0.31	
Decylaldehyde (14)	0.53[a]	0.10	−0.31	0.01	−0.07	0.08	0.03	−0.13	−0.24	0.06	0.18	0.20	0.56[a]

[a]99% confidence levels.

2-butanone and benzaldehyde. These compounds possibly mainly derived from vehicular exhaust.

Good correlations between formaldehyde, acetaldehyde and other carbonyls had been found in Guangzhou before (Feng et al., 2004). The difference of correlations between both studies might be due to the differences of sampling sites and time. The sampling time of present study was 11:00 a.m.–13:00 p.m. from June to September in summer. The temperature during sampling was 30–38 °C. Therefore, the photooxidation would be very strong. Formaldehyde could be mainly produced by photochemical reactions of some VOCs and also removed by photolysis and reaction with OH at the same time. The sampling of the previous study (Feng et al., 2004) was performed at 8:00 p.m.–12:00 p.m. from August to September in the same district. At that period, the main source might be vehicular exhaust and the photochemical reactions might contribute only a small part of carbonyl compounds. Possanzini et al. (1996) also observed that vehicular exhaust was the primary source in winter while both vehicular exhaust and photochemical reactions were the major sources in summer. In HongKong, correlations between carbonyls were also found to be good in the winter and bad for the one-year monitoring (Ho et al., 2002). All the studies above indicated that photochemical reactions were one of the most important sources of carbonyl compounds in summer, especially at noon.

4. Conclusion

Atmospheric levels of carbonyl compounds and their possible sources in urban area of Guangzhou were measured in this study. The total concentrations of carbonyls were highest in the residential area (Liwan District), followed by the downtown area, the industrial area, the Botanical Garden and the semi-rural area. Acetone was the most abundant carbonyl in the ambient air, accounting for 24–40% of the total carbonyls. Acetone, formaldehyde and acetaldehyde were the dominated carbonyls and accounted for 63–72% of the total carbonyls. The long lifetime of acetone resulted in higher concentrations in the atmosphere. Good correlations between acetaldehyde, propionaldehyde, 2-butanone, butyraldehyde and benzaldehyde indicated that they came from the same source, e.g. vehicular exhaust. Formaldehyde had bad correlations with other carbonyls, indicating that photochemical reactions might be another important source at noon in summer other than primary emissions from vehicular exhaust. Cooking exhaust from all kinds of restaurants might be the major source of high-molecular weight aldehydes in urban air. The mean concentrations of carbonyl compounds in five districts had no pronounced differences, which was possibly due to the ease mixture and dispersion of the compounds in summer.

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