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## Spatiotemporal distribution of carbonyl compounds in China

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## ABSTRACT

A sampling campaign was carried out at nine Chinese cities in 2010/2011. Fifteen monocarbonyls (C# = 1–9) were quantified. Temperature is the rate-determining factor of the summertime carbonyl levels. The carbonyl emissions in winter are mainly driven by the primary anthropogenic sources like automobile. A molar ratio of propionaldehyde to nonaldehyde is a barometer of the impact of atmospheric vegetation emission which suggesting that strong vegetation emissions exist in summer and high propionaldehyde abundance is caused by fossil fuel combustion in winter. Potential health risk assessment of formaldehyde and acetaldehyde was conducted and the highest cumulative risks were observed at Chengdu in summer and Wuhan in winter. Because of the strong photochemical reaction and large amount of anthropogenic emissions, high concentrations of carbonyl compounds were observed in Chengdu. The use of ethanol-blended gasoline in Wuhan is the key reason of acetaldehyde emission and action should be taken to avoid potential health risks.

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## 1. Introduction

Carbonyl compounds originate from both primary and secondary origin. The compounds can be emitted either directly from incomplete combustion of biomass and fossil fuel or formed indirectly from the photochemical oxidations of volatile organic compounds (VOCs) in both of natural and anthropogenic sources (Possanzini et al., 2002). Industrial emissions and vehicular exhausts were identified to be the primary sources of carbonyl compounds in urban areas (Ho et al., 2007, 2013). Increasing evidences suggest that cooking fumes (e.g. meat cooking or cooking oils) can release large amounts of high molecular weight carbonyls (Feng et al., 2005; Schauer et al., 2002). Other studies reported that aldehydes generate from secondary emission can be more than from primary emission (Altshuller, 1993). The lifetimes of carbonyls

in troposphere are different due to their various physicochemical properties and the production/removal pathways (DeMore et al., 1992). A long range transport of carbonyls and their precursors can lead to enhanced photochemical pollution in the metropolitan areas (Possanzini et al., 2002).

Several carbonyls have been recognized for their adverse human health effects due to their potential carcinogenic and mutagenic properties (CEPA, 1993; NCR, 1981; WHO, 1987), in addition of their capability of forming toxic and phytotoxic radical intermediates or stable species (Roberts, 1990). Specific carbonyls induced adverse human health effect symptoms are eyes and lung irritations (WHO, 2000). Formaldehyde is classified as Group 1 human carcinogen by the International Agency for Research on Cancer (IARC) for its carcinogenicity (IARC, 2006) and acetaldehyde is a suspected carcinogen (Baez et al., 2003; Zhang et al., 1994). Formaldehyde can cause nasopharyngeal cancer (IARC, 2004) and is suggested to be potentially associated with leukemia (Zhang et al., 2009). World-wide scientific community has been focusing on pollution level, potential sources and human exposure of carbonyls in indoor and outdoor environment ever since (Baez et al., 2003; Cavalcante et al.,

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2006; Feng et al., 2004; Gilbert et al., 2006; Marchand et al., 2006; Zhang et al., 1994).

Airborne carbonyls have been investigated at urban areas in China (Cheng et al., 2014; Ho et al., 2014; Liu et al., 2013; Louie et al., 2013; Weng et al., 2009), nonetheless only limited studies had been conducted in middle and western regions despite of rapid urbanization and industrialization in these regions. There are also lack of information about high molecular weight carbonyls (HMW carbonyls,  $C\#>6$ ) in urban atmosphere (Chi et al., 2007; Huang et al., 2008; Wang et al., 2010). Emission from vegetation can be one of possible sources induced by ozone exposure of plants (Karl et al., 2005). Biomass, biofuel and charcoal combustion are other sources of HMW carbonyls in air (Andreae and Merlet, 2001). In the densely populated urban areas, higher HMW carbonyls emissions would be expected due to the increased consumption of fuels and large emission from industries which seriously hamper air quality in urban areas.

The aim of this study is to quantify ambient monocarbonyls and characterize their seasonal and spatial variations in urban and rural areas of China. The inhalation cancer risk of carbonyls is used to compare the potential health impact of carbonyl among different Chinese cities.

## 2. Experimental

A national wide survey of ambient monocarbonyl compounds were conducted simultaneously in nine sites during summer and winter season. Fifteen carbonyls in ambient air were sampled using standard 2,4-dinitrophenylhydrazine (DNPH) derivatization method followed by high-performance liquid chromatography (HPLC) analysis (USEPA, 1999) to elucidate the condition of airborne carbonyl pollution in China.

### 2.1. Sampling site

Nine sampling sites in different regions (covering an area of 23–39°N, 91–121°E) of China were selected to represent economically-developed and economically-developing cities. The seven urban sampling sites include Beijing [BJ], Chengdu [CD], Guangzhou [GZ], Shanghai [SH], Wuhan [WH], Xiamen [XM], and Yantai [YT] while the two rural sites were chosen to be Qinghai Lake, Qinghai [QH] and Lasa, Tibet [TB]. The details of sampling

locations are described in Table 1. Samplers were located on rooftops at ~10–20 m above ground level for two weeks during summer (August 2010) and winter (January 2011), respectively.

### 2.2. Sample collection

A 24-h interval integrated samples (from 10:00 a.m. onwards) were collected daily in this study. Air samples were collected in silica cartridges impregnated with acidified 2,4-dinitrophenylhydrazine (DNPH) (Sep-Pak DNPH-silica, 55–105  $\mu\text{m}$  particle size, 125 Å pore size; Waters Corporation, Milford, MA) at flow rate of 0.7 L  $\text{min}^{-1}$ . Total 127 and 130 samples were collected in summer and winter, respectively. Collection efficiencies were measured under different field conditions by sampling carbonyls into two identical cartridges connected in series. They were calculated as  $100\%(1 - A_b/A_f)$ , where  $A_f$  and  $A_b$  were the amounts of carbonyl collected on the front and the back sampling tubes, respectively. No detectable breakthrough was found at these sampling flow rates and sampling times. The flow rates were checked at the field from start and end of each sampling period using a calibrated flow meter (Gilibrator Calibrator; Gilian Instruments, W. Caldwell, NJ). A Teflon filter assembly (Whatman, Clifton, NJ) with an ozone scrubber (Sep-Pak; Waters Corporation) was installed in front of the DNPH-silica cartridge in order to remove any particulate matters and prevent possible disturbance from ozone (Spaulding et al., 1999). Collocated samples were collected to examine the collection reproducibility (>95%) in the field for all of the samplers. One cartridge was reserved as a field blank on each sampling trip and was handled in same manner as the other sample cartridges. The amounts of carbonyls detected in the cartridges were corrected for field blank under air concentrations of the carbonyls analysis. The DNPH-coated cartridges were stored in a refrigerator at <4 °C after sampling and before analysis. Different meteorological parameters such as temperature, air pressure, relative humidity (RH), rainfall, and wind speed and direction were recorded during the sampling period.

### 2.3. Analytical methods

A total of 15 carbonyls were quantified, including formaldehyde (C1), acetaldehyde (C2), propionaldehyde (C3), *iso* + *n*-butyraldehyde (*iso* + *n*C4), benzaldehyde (*benz*), *iso*-valeraldehyde (*iso*-C5), *n*-valeraldehyde (*n*C5), *o*-tolualdehyde (*o*-tol), *m*-tolualdehyde (*m*-tol), *p*-tolualdehyde (*p*-tol), hexaldehyde (C6), 2,5-dimethylbenzaldehyde (2,5-DB), heptaldehyde (C7), octaldehyde (C8) and nonaldehyde (C9). Unsaturated carbonyls including acrolein and crotonaldehyde were detected but not reported in the study. The unsaturated carbonyl DNP-hydrazones could react with excess reagent to form adducts, leading to ambiguity in accurate quantification due to chromatographic interferences (e.g. double peaks) and response factor issues (Ho et al., 2011; Schulte-Ladbeck et al., 2001). In-laboratory experiments demonstrated that the collection efficiencies were  $>93 \pm 5\%$  for all target carbonyls under the same flow rate, temperature and RH.

Each DNPH-coated cartridge was eluted with 2.0 mL acetone-free acetonitrile (HPLC/GCMS grade, J&K Scientific Ltd., Ontario, Canada) solution and transferred to a volumetric flask. Previous studies demonstrated that neither DNPH nor DNPH derivatives remained in the cartridge after 2.0 mL acetone-free acetonitrile solution elution (Ho et al., 2007). Certified calibration standards of the monocarbonyl DNP-hydrazones were purchased from Supelco (Bellefonte, PA) and diluted in concentration ranges of 15–3000  $\mu\text{g mL}^{-1}$ . The calibration solutions were allowed to stand at room temperature for 6 h for complete derivatization. The final volume of each calibration solution was filled up to 2.0 mL with 8:2

**Table 1**  
Sampling site description in nine cities.

City	Population (million)	Description	Latitude	Longitude	Height <sup>a</sup> (m)
Beijing	19.6	Capital of China	39°58' N	116°23' E	14
Chengdu	14.0	Continental & industrial	30°39' N	104°1' E	15
Guangzhou	12.7	Industrial & commercial	23°7' N	113°21' E	10
Shanghai	23.0	Industrial & commercial	31°18' N	121°30' E	20
Wuhan	9.8	Industrial & commercial	30°31' N	114°21' E	10
Xiamen	3.5	Coastal & commercial	24°28' N	118°5' E	8
Yantai	7.0	Coastal & commercial	37°28' N	121°26' E	10
Lasa, Tibet	0.6	Continental & plateau	29°38' N	91°2' E	15
Qinghai Lake	0.1	Rural area & plateau	36°58' N	99°53' E	12

<sup>a</sup> Height of air inlet of the sampler above the ground.

(v/v) of acetonitrile/pyridine (HPLC/GCMS grade, Sigma) concentration ratio. The calibration curve was linearized and correlation of determination ( $r^2$ ) was >0.999. The calibration standards and cartridge extracts were analyzed by injecting 20  $\mu\text{L}$  of the solution to high-pressure liquid chromatography (HPLC) system (Series 1200; Agilent Technology, Santa Clara, CA) coupled with photodiode array detector (DAD). A reversed-phase separation column ( $4.6 \times 250$  mm Spheri-5 ODS 5  $\mu\text{m}$  C-18, PerkinElmer, Norwalk, CT) was installed in the HPLC system and operated at room temperature (25 °C). The mobile phase consisted of three solvent mixtures: mixture A, 6:3:1 (v/v) of water/acetonitrile/tetrahydrofuran; mixture B, 4:6 (v/v) of water/acetonitrile; and mixture C, acetonitrile. The gradient program was operated firstly (80% A)/(20% B) for 1 min, secondly at linear gradient of (50% A)/(50% B) in 8 min, thirdly (100% B) in 10 min, fourthly (100% C) in 6 min, and finally (100% C) in 5 min. The flow rate was 2.0 mL  $\text{min}^{-1}$  throughout the run. The absorbance of 360 and 390 nm wavelength was applied for identifying aliphatic and aromatic carbonyls (e.g. benzaldehyde and tolualdehydes) respectively. Identification and quantification of carbonyl compounds were based on retention time and peak area integration of different carbonyl compounds, respectively. The minimum detection limit (MDL) was estimated by analyzing a minimum of seven replicates of a standard solution containing the analytes at a concentration of 0.015  $\mu\text{g mL}^{-1}$ . It is estimated using the equation

$$\text{MDL} = t_{(n-1, 1-\alpha=99\%)} \times S$$

in which  $t_{(n-1, 1-\alpha=99\%)}$  is the student's  $t$ -distribution value at  $n - 1$  degrees of freedom and  $S$  is the standard derivation of the replicates. The MDLs of the target carbonyls ranged from 0.002 to 0.010  $\text{ng } \mu\text{L}^{-1}$  in which can be translated to 0.016–0.12 ppbv with sampling volume of 2.02  $\text{m}^3$ . Four key attributes such as value, precision, accuracy, and validity were obeyed throughout measurements. Quality assurance is an essential part of the measurement process, which provides precision, accuracy, and validity estimate and guarantee that these attributes are within acceptable limit. Quality assurance program encompasses quality control (QC) and quality assurance (QA). QC activities are continuous measurement activities and data processing done by specific personnel. A standard operating procedure is composed after sample collection, sample analysis, and data processing. This procedure provides guideline on calibration and performance test requirement (e.g. number of blank and replicate analysis). The procedure also includes tolerance level and contingency plan when this level is exceeded in any circumstances. QC activities consist of equipment maintenance, acceptance testing, operational training, and support. The measurement precision is a range of 0.5–3.2% for the measured carbonyls.

#### 2.4. Risk calculation model

The inhalation cancer risk for carbonyls is calculated by using the following equation:

$$R_{ij} = E_{ij} \times \text{IUR}_j \quad (1)$$

where,  $R_{ij}$  is used to denote estimated inhalation cancer risk of chemical  $j$  at each sampling site  $i$ ,  $E_{ij}$  is use to measure exposure concentration of chemical  $j$  at each sampling site  $i$ , and  $\text{IUR}_j$  is used to denote Inhalation Unit Risk ( $\text{m}^3 \mu\text{g}^{-1}$ ) for chemical  $j$ . IUR values are obtained from the U.S. EPA's Integrated Risk Information System (IRIS) (USEPA, 2012). The IUR represents excess cancer risk over background to a pollutant and is typically expressed as risk or probability of cancer for 70-yr exposure per 1  $\mu\text{g}$  pollutant in cubic

meter ( $\text{m}^{-3}$ ) air (USEPA, 1986). The cumulative cancer risk is the summation of available individual compound risk and shown in equation (2).

$$\text{CR}_i = \sum_j R_{ij} \quad (2)$$

where  $R_{ij}$  is the estimated inhalation cancer risk in chemical  $j$  in each sampling site  $i$ , and  $\text{CR}_i$  is the estimate cumulative cancer risk in each sampling site  $i$ . In this study, we focused on cancer risks associated with outdoor exposure only and compare the cumulative cancer risk among different cities.

### 3. Results and discussion

#### 3.1. Characterization of carbonyl compounds

The average concentrations and statistical summary of the fifteen carbonyl compounds (in ppbv) are shown in Table 2. Large variations were observed among the nine sampling sites. The total concentrations of the quantified carbonyls ranged from 0.71 to 32.1 ppbv (average: 8.71 ppbv) in summer and from 0.24 to 16.5 ppbv (average: 4.63 ppbv) in winter. This variability indicates large spatial and temporal differences of the carbonyls levels in China since the measurement sites are scattered across the country. Emissions from motor vehicles and industries are the major source of carbonyls in urban areas in China. Formaldehyde and acetaldehyde are the most abundant carbonyls produced from either diesel- or gasoline-fueled vehicles (Ho et al., 2007, 2012). Despite the pollutants transported from upwind source areas and formed from atmospheric photo-oxidation reactions, biomass burning and vegetative emission are also the potential sources of carbonyls in rural areas in China. Average concentrations in summer are higher than those in winter for most of the target carbonyls. This can be attributed to warmer weather that favors volatilization of aldehydes or secondary formation from their precursors. Formaldehyde was the most abundant carbonyl species detected in all cities, ranged from 0.42 to 17.5 ppbv (average 5.07 ppbv), and 0.07 to 5.84 ppbv (average 2.04 ppbv) in summer and winter, respectively. Acetaldehyde was the second most abundant carbonyls followed by nonaldehyde in summer and propionaldehyde in winter. The

**Table 2**

The average concentrations and statistical summary of 15 carbonyls in summer and winter (in ppbv).

Compounds	Summer ( $n = 127$ )			Winter ( $n = 127$ )		
	Range	Average	S.D.	Range	Average	S.D.
Formaldehyde (C1)	0.42–17.5	5.07	4.11	0.07–5.8	2.04	1.53
Acetaldehyde (C2)	0.18–9.46	1.91	1.54	0.01–6.21	1.42	1.18
Propionaldehyde (C3)	bd–0.93	0.25	0.21	bd–0.74	0.17	0.14
iso + n-Butyraldehyde (iso + nC4)	0.01–0.75	0.16	0.14	0.01–0.19	0.05	0.03
Benzaldehyde (benz)	0.01–1.83	0.18	0.27	bd–0.35	0.07	0.06
iso-Valeraldehyde (iso-C5)	0.01–0.81	0.17	0.17	bd–0.76	0.12	0.13
n-Valeraldehyde (nC5)	bd–0.42	0.05	0.06	bd–0.19	0.03	0.03
o-Tolualdehyde (o-tol)	bd	bd	bd	bd	bd	bd
m-Tolualdehyde (m-tol)	bd–0.06	0.02	0.02	bd–0.04	0.01	0.01
p-Tolualdehyde (p-tol)	bd–0.03	0.01	0.01	bd–0.04	0.01	0.01
Hexaldehyde (C6)	bd–0.97	0.16	0.15	bd–0.50	0.07	0.07
2,5-Dimethylbenzaldehyde (2,5-DB)	bd–0.11	0.02	0.02	bd–0.05	0.01	0.01
Heptaldehyde (C7)	bd–0.86	0.16	0.13	0.01–0.31	0.06	0.05
Octaldehyde (C8)	bd–1.15	0.20	0.18	0.01–0.17	0.06	0.04
Nonaldehyde (C9)	bd–2.10	0.42	0.41	0.02–0.51	0.14	0.10
Total	0.71–32.1	8.71	6.90	0.24–16.5	4.63	3.50

Remarks: bd represents below limit of detection.

aggregate of formaldehyde and acetaldehyde contributed up to average 81% and 74% of the total quantified carbonyls in summer and winter, respectively. These results are consistent with other studies which illustrate that formaldehyde and acetaldehyde are the two most abundant carbonyls in the ambient air at many Chinese cities (Dai et al., 2012; Ho et al., 2002; Lu et al., 2010; Mu et al., 2007; Yuan et al., 2012). High concentrations of HMW carbonyls (e.g. C6, C7, C8 and C9) were observed at all measurement sites. Among these HMW carbonyls, nonaldehyde was the most abundant species during both seasons (summer: 0.42 ppbv; winter: 0.14 ppbv), followed by octaldehyde (0.20 ppbv) in summer and hexaldehyde (0.07 ppbv) in winter. These four HMW carbonyls accounted for 11% and 7% of the total quantified carbonyls in summer and winter, respectively.

### 3.2. Seasonal and spatial variation

Table 3 shows the average concentrations of individual carbonyl compounds measured at all sites during summer and winter. The average concentration of total carbonyl compounds was significantly high in summer at all sampling sites except for TB and XM. This could be attributed to the following reasons 1) There are stronger photochemical activities in summer than in winter. Photochemical reaction is one of the predominant sources of these carbonyls and the relatively high solar radiation, high relative humidity (RH) and temperature prompt photochemical reactions possibly explaining the enhancement of carbonyl concentrations. (Ceron et al., 2007; Ho et al., 2002; Li et al., 2010). The high RH might be in favor of HONO formation, which acts as an initiator to

photochemistry (Atkinson, 2000) and might be the cause for the elevation of carbonyl concentrations (Pang and Mu, 2006). 2) Large vegetation emissions are also contributed towards high summer-time carbonyl. It was reported that emission from plants were another major source of HMW carbonyl compounds, especially when the plants are attacked by insect or exposed to ozone (Karl et al., 2005; Wildt et al., 2003). The lower molar ratio of propionaldehyde to nonaldehyde ( $C_3/C_9$ ) indicates that vegetation has large influences on summer carbonyl levels. 3) High temperature also favors the volatilization of carbonyl compounds (particularly formaldehyde) and their precursors from adhesive and paint on building materials.

Distinct seasonal variations (summer vs. winter) of individual carbonyl compounds were observed in this study. High summer to winter molar ratios (S/W ratio > 1) of formaldehyde and acetaldehyde at the northern cities (BJ, QH and YT) are due to low concentrations of carbonyls in winter. These results are consistent with depressed photochemical activity, low vegetation emission, and low volatilization (e.g. low temperature) in the winter observed at north China. Miller et al. (2008) reported that atmospheric formaldehyde and acetaldehyde being reduced in winter is due to inactive photo-oxidation of VOCs. Fig. 1 demonstrates that the fractional differences of formaldehyde between summer and winter are higher in the northern cities (BJ, QH and YT) than in the southern cities (GZ and XM). The increased photo-oxidations of VOCs can be an explanation for the elevation of formaldehyde abundance in summer (Duane et al., 2002; Shepson et al., 1991). This indicates that both photochemical activity and temperature play important roles in the formation of formaldehyde during

**Table 3**  
Average concentrations of carbonyl compounds in nine Chinese sites in summer and winter (ppbv).

City	BJ	CD	GZ	QH	SH	TB	WH	XM	YT
<i>Summer</i>									
C1	8.35 ± 3.34	11.4 ± 3.80	6.69 ± 1.98	1.54 ± 0.51	4.69 ± 2.33	1.72 ± 0.18	7.43 ± 4.14	0.83 ± 0.31	3.90 ± 1.12
C2	3.05 ± 0.99	3.09 ± 1.05	2.28 ± 0.77	0.29 ± 0.07	1.72 ± 0.94	0.87 ± 0.18	3.82 ± 2.19	0.32 ± 0.13	1.97 ± 0.77
C3	0.43 ± 0.14	0.47 ± 0.18	0.32 ± 0.11	0.03 ± 0.02	0.21 ± 0.11	0.15 ± 0.16	0.45 ± 0.24	0.01 ± 0.01	0.15 ± 0.08
iso + nC4	0.25 ± 0.09	0.26 ± 0.09	0.20 ± 0.06	0.03 ± 0.01	0.17 ± 0.08	0.07 ± 0.01	0.35 ± 0.23	0.03 ± 0.01	0.09 ± 0.03
Benz	0.17 ± 0.05	0.26 ± 0.09	0.23 ± 0.07	0.01 ± 0.00	0.18 ± 0.08	0.05 ± 0.01	0.69 ± 0.56	0.01 ± 0.01	0.05 ± 0.03
iso-C5	0.22 ± 0.07	0.36 ± 0.12	0.40 ± 0.19	0.01 ± 0.01	0.11 ± 0.07	0.04 ± 0.01	0.17 ± 0.11	0.02 ± 0.01	0.18 ± 0.21
nC5	0.09 ± 0.02	0.09 ± 0.04	0.05 ± 0.02	0.01 ± 0.00	0.04 ± 0.02	0.03 ± 0.01	0.15 ± 0.09	bd	0.03 ± 0.01
o-Tol	bd	bd	bd	bd	0.01 ± 0.00	bd	bd	bd	0.01 ± 0.00
m-Tol	0.03 ± 0.01	0.03 ± 0.02	0.03 ± 0.01	bd	0.02 ± 0.01	bd	0.03 ± 0.02	bd	0.02 ± 0.02
p-Tol	0.02 ± 0.01	0.01 ± 0.01	0.02 ± 0.01	bd	0.01 ± 0.00	bd	0.01 ± 0.01	bd	bd
C6	0.21 ± 0.05	0.26 ± 0.10	0.13 ± 0.03	0.02 ± 0.01	0.12 ± 0.05	0.05 ± 0.01	0.41 ± 0.21	bd	0.08 ± 0.03
2,5-DB	0.02 ± 0.01	0.04 ± 0.01	0.05 ± 0.02	bd	0.02 ± 0.01	0.01 ± 0.01	0.03 ± 0.02	bd	0.02 ± 0.01
C7	0.21 ± 0.05	0.26 ± 0.10	0.17 ± 0.04	0.02 ± 0.01	0.16 ± 0.08	0.08 ± 0.03	0.33 ± 0.18	0.01 ± 0.01	0.18 ± 0.16
C8	0.25 ± 0.05	0.30 ± 0.17	0.11 ± 0.03	0.04 ± 0.01	0.27 ± 0.14	0.11 ± 0.06	0.49 ± 0.25	0.01 ± 0.01	0.11 ± 0.03
C9	0.52 ± 0.16	0.86 ± 0.48	0.27 ± 0.08	0.14 ± 0.03	0.58 ± 0.23	0.21 ± 0.14	1.06 ± 0.48	0.02 ± 0.02	0.16 ± 0.07
<b>Total</b>	<b>13.8 ± 4.61</b>	<b>17.7 ± 5.49</b>	<b>11.0 ± 3.23</b>	<b>2.16 ± 0.63</b>	<b>8.29 ± 4.02</b>	<b>3.33 ± 0.56</b>	<b>15.4 ± 8.08</b>	<b>1.27 ± 0.46</b>	<b>6.93 ± 2.23</b>
<i>Winter</i>									
C1	1.39 ± 0.74	3.62 ± 0.86	3.35 ± 1.38	0.27 ± 0.16	1.99 ± 0.70	1.55 ± 1.09	4.57 ± 1.16	1.22 ± 0.43	1.17 ± 0.74
C2	1.01 ± 0.72	2.29 ± 0.69	1.59 ± 0.51	0.17 ± 0.14	1.30 ± 0.67	1.19 ± 0.99	4.19 ± 0.91	0.69 ± 0.27	1.33 ± 0.78
C3	0.13 ± 0.09	0.29 ± 0.07	0.18 ± 0.06	0.03 ± 0.01	0.16 ± 0.06	0.16 ± 0.13	0.48 ± 0.12	0.06 ± 0.03	0.15 ± 0.09
iso + nC4	0.03 ± 0.02	0.07 ± 0.02	0.05 ± 0.02	0.02 ± 0.01	0.05 ± 0.01	0.05 ± 0.03	0.12 ± 0.03	0.04 ± 0.02	0.05 ± 0.02
Benz	0.05 ± 0.03	0.14 ± 0.05	0.09 ± 0.03	0.01 ± 0.01	0.07 ± 0.04	0.05 ± 0.04	0.19 ± 0.06	0.03 ± 0.01	0.06 ± 0.03
iso-C5	0.07 ± 0.04	0.33 ± 0.19	0.18 ± 0.08	0.02 ± 0.01	0.12 ± 0.06	0.06 ± 0.05	0.26 ± 0.12	0.04 ± 0.01	0.09 ± 0.06
nC5	0.03 ± 0.01	0.06 ± 0.01	0.03 ± 0.01	0.01 ± 0.00	0.03 ± 0.01	0.03 ± 0.02	0.10 ± 0.04	0.02 ± 0.01	0.02 ± 0.01
o-Tol	bd	bd	bd	bd	bd	bd	bd	bd	bd
m-Tol	0.01 ± 0.00	0.01 ± 0.01	0.01 ± 0.00	bd	0.02 ± 0.01	0.01 ± 0.01	0.02 ± 0.01	0.01 ± 0.00	0.01 ± 0.00
p-Tol	bd	bd	0.01 ± 0.00	bd	0.01 ± 0.00	0.01 ± 0.01	0.01 ± 0.00	bd	0.01 ± 0.00
C6	0.05 ± 0.02	0.12 ± 0.03	0.07 ± 0.02	0.01 ± 0.01	0.08 ± 0.03	0.04 ± 0.03	0.26 ± 0.10	0.02 ± 0.01	0.05 ± 0.02
2,5-DB	0.01 ± 0.00	0.02 ± 0.01	0.01 ± 0.01	bd	0.01 ± 0.00	0.01 ± 0.01	0.02 ± 0.01	0.01 ± 0.00	0.01 ± 0.00
C7	0.04 ± 0.02	0.08 ± 0.02	0.04 ± 0.01	0.02 ± 0.01	0.06 ± 0.01	0.05 ± 0.03	0.14 ± 0.04	0.02 ± 0.01	0.11 ± 0.08
C8	0.05 ± 0.01	0.10 ± 0.02	0.05 ± 0.02	0.02 ± 0.02	0.08 ± 0.02	0.05 ± 0.02	0.11 ± 0.05	0.03 ± 0.01	0.06 ± 0.03
C9	0.11 ± 0.06	0.29 ± 0.05	0.11 ± 0.04	0.07 ± 0.06	0.22 ± 0.06	0.09 ± 0.04	0.29 ± 0.12	0.06 ± 0.03	0.09 ± 0.06
<b>Total</b>	<b>3.15 ± 1.81</b>	<b>8.45 ± 2.24</b>	<b>6.39 ± 2.40</b>	<b>0.71 ± 0.38</b>	<b>4.79 ± 2.07</b>	<b>3.43 ± 2.55</b>	<b>11.4 ± 2.39</b>	<b>2.33 ± 0.71</b>	<b>3.35 ± 1.77</b>

Remarks: "bd" represents below minimum of detection.

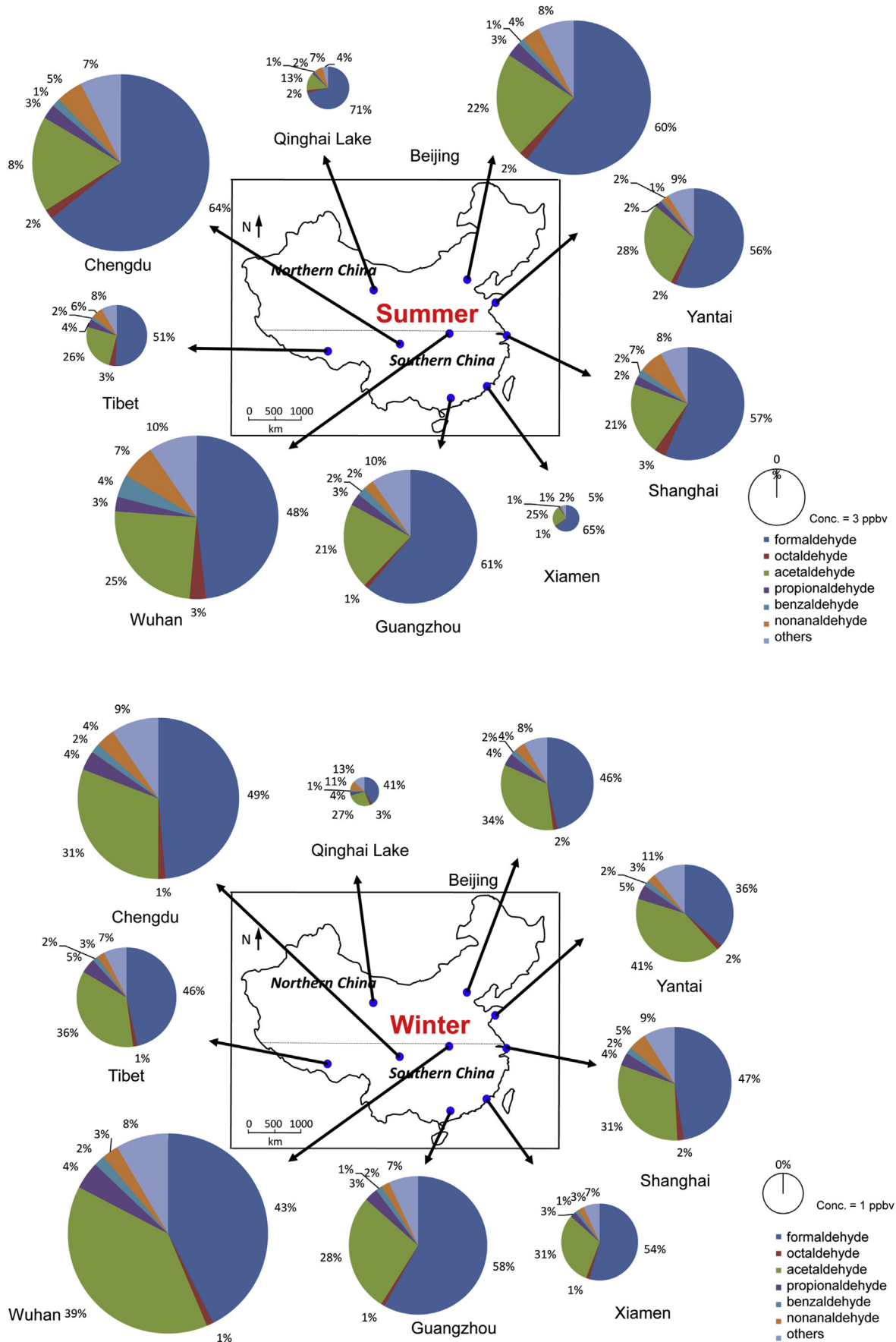


Fig. 1. Average carbonyl compositions in nine cities.

summer. The S/W ratios for the other carbonyls were close to 1 or >1 in all cities except XM. Acetaldehyde, propionaldehyde and isovaleraldehyde are in general had the lowest S/W ratio at most cities. These three compounds are the most abundant carbonyls emitted from automobiles and industries (Grosjean et al., 2001; Kean et al., 2001) which can be accumulated in the atmosphere with limited sinks (i.e. photo-oxidation by  $\cdot\text{OH}$  radical and photolysis (Christensen et al., 2000)) in winter.

As shown in Table 3, the total measured carbonyls were found to be most abundant in CD (17.7 ppbv) followed by WH (15.4 ppbv) in summer and in WH (11.4 ppbv) followed by CD (8.45 ppbv) in winter, respectively. Wuhan is the capital of Hubei province and Chengdu is the capital of Sichuan Province. Both of the cities are the top ten most populous cities in China. There are approximately 10 million and 14 million people in the metropolitan area of Wuhan and Chengdu, respectively. Wuhan's major industries include optoelectronics, automobile and steel manufacturing, chemical and power plants. The city is a natural resources hub of China (e.g. land, water, and air transportation). Chengdu is located at a basin-like topography with low wind speed and stable atmospheric condition and the major industries include coal-fired power plants, chemical plants, metallurgy and building materials plants. The major contributing sources of air pollution in Wuhan and Chengdu are motor vehicles and the use of coal for heating and different industrial processes. Because of the strong photochemical reaction and large amount of industrial emissions, high concentrations of carbonyl compounds were observed in Chengdu and Wuhan in summer. Formaldehyde was the most abundant specie found in these cities followed by acetaldehyde and the highest average concentration of formaldehyde was observed in CD (11.4 ppbv), followed by BJ (8.35 ppbv) and WH (7.43 ppbv) during summer. These values are higher than those reported in rural areas (e.g. Waliguan (4.16 ppbv), and Pearl River Delta (PRD) (3.54–6.26 ppbv) (Mu et al., 2007; Yuan et al., 2012)). However, but the values are closer to those reported in urban Beijing (5.54–8.72 ppbv) (Li et al., 2010). The highest average concentration of acetaldehyde was observed in WH (summer: 3.82 ppbv; winter: 4.19 ppbv) at both seasons.

Ethanol-blended gasoline (E-gasoline) has been using in fleet vehicles in recent years and in the nine related provinces (i.e. a total of 27 cities include WH and the surrounding cities of YT), all gasoline is sold in an addition of 10% (v/v) ethanol (Pang et al., 2008). E-Gasoline is widely used as an alternative fuel in some countries such as Brazil, United States, European Union, Canada and Thailand (Leong et al., 2002; Magnusson et al., 2002) to reduce CO and particulate matter emissions and carbonyls may be formed by using E-gasoline. Pouloupoulos et al. (2001) investigated the air pollutant emissions from gasoline engine and found that acetaldehyde emission was appreciably increased for ethanol-containing fuel. Pang et al. (2008) found that in gasoline engine tailpipe emissions, total carbonyls from E10 were 3.0–61.7% higher than those from gasoline. YT contains the highest acetaldehyde fraction among the nine sites (summer: 28%; winter: 41%). High concentration of acetaldehyde observed in WH and YT can be due to the addition of ethanol in gasoline leading to higher acetaldehyde emission.

The lowest concentrations of the total measured carbonyls were observed in XM (summer: 1.27 ppbv; winter: 2.33 ppbv) and QH (summer: 2.16 ppbv; winter: 0.71 ppbv) in both seasons. XM is a subtropical climate city in southeastern China, with less anthropogenic emission compare to other mega cities. Clean air mass coming from the oceans could dilute ambient air pollutants to a great extent during marine monsoon seasons. So the total measured carbonyls in Xiamen were very limited during summer. QH is located at lake region with low population, less anthropogenic emissions may result in low loadings in the samples.

Formaldehyde was also the most abundant species found in these two cities and the lowest concentration was observed in XM (0.83 ppbv) during summer and QH (0.27 ppbv) in winter. These concentrations are lower than those reported at Ma Zhuang (1.5 ppbv), a rural area at eastern China during summer (Wang et al., 2010).

For HMW carbonyls (C6–C9), all species show consistent seasonal variation with lower concentrations in winter but higher concentrations in summer at all cities except XM. This observation is in accordance with studies at other locations. For example, measurements at Helsinki showed that the summertime levels of HMW carbonyls (C6–C11) were 2–4 times higher than those observed in wintertime. Like many other semi-volatile hydrocarbons, the HMW carbonyls (with low vapor pressure) are more likely to condense on the particulate matter (PM) in winter (Grosjean et al., 1996) leading to low concentrations of gas-phase HWM carbonyls as observed in winter in this study. The highest concentration of nonaldehyde was observed in WH (summer: 1.06 ppbv; winter: 0.29 ppbv) and CD (summer: 0.86 ppbv; winter: 0.29 ppbv), followed by SH (summer: 0.58 ppbv; winter: 0.22 ppbv). However, in rural or coastal areas (QH, XM and YT), the molar contribution of HMW carbonyls was higher in winter than in summer suggesting additional sources of HMW carbonyls in these regions in winter. It is noted that in wintertime both vegetation emission and the oxidizing capacity are minimized and that the HMW carbonyls are determined mostly by anthropogenic sources. These sources can be locally emitted or transported from urban or industrial areas.

In addition, carbonyl concentrations in atmosphere can be affected by numerous factors such as direct primary emissions, secondary formations, meteorological conditions and carbonyl sinks (e.g. photolysis of these carbonyls generated hydroxyl radicals ( $\cdot\text{OH}$ ) and caused dry deposition) (Anderson et al., 1996; Pang and Mu, 2006).

### 3.3. Carbonyl ratios as source indicators

The molar ratios of formaldehyde/acetaldehyde ( $C_1/C_2$ ) were determined in nine sites (Table 4). The  $C_1/C_2$  ratio has been widely used as an indicator of possible sources for formaldehyde (Shepson et al., 1991) which usually varies from ~1 to 2 for urban areas and up

**Table 4**  
The molar ratios of formaldehyde/acetaldehyde ( $C_1/C_2$ ) in nine sampling sites.

Location		Formaldehyde/ acetaldehyde $C_1/C_2$			Propionaldehyde/ nonaldehyde $C_3/C_9$		
		Mean	Min	Max	Mean	Min	Max
Winter	BJ	1.54	1.13	2.13	1.29	0.34	3.64
	CD	1.64	0.95	2.06	1.02	0.72	1.50
	GZ	2.04	1.01	2.53	1.63	0.94	2.24
	QH	2.71	0.93	15.7	0.42	0.07	0.74
	SH	1.62	1.09	2.28	0.77	0.49	2.56
	TB	1.42	0.94	1.66	1.70	0.73	3.46
	WH	1.11	0.70	1.48	1.91	0.71	3.02
	XM	1.81	0.79	2.33	0.94	0.34	1.51
	YT	0.87	0.15	1.49	2.32	0.44	6.30
Summer	BJ	2.77	1.01	5.05	0.80	0.32	1.19
	CD	3.80	1.77	5.24	0.61	0.39	0.99
	GZ	2.99	1.83	3.48	1.21	0.52	1.56
	QH	5.31	3.44	8.11	0.24	0.10	0.57
	SH	2.82	2.33	3.78	0.35	0.20	0.66
	TB	2.05	1.48	2.50	0.92	0.02	4.29
	WH	1.92	0.80	2.52	0.41	0.24	0.60
	XM	2.63	1.63	3.15	0.88	0.20	2.56
	YT	2.06	1.67	2.70	0.95	0.34	1.75

to ~10 for rural sites (Possanzini et al., 1996; Shepson et al., 1991). Higher  $C_1/C_2$  ratio implies that the photo-oxidation of natural hydrocarbons such as isoprene yields more formaldehyde than acetaldehyde (Duane et al., 2002; Shepson et al., 1991), even though few studies argue that the ratios often have large variations because of the differences in the pollution sources and meteorological conditions (Grosjean, 1992). In the present study, the  $C_1/C_2$  ratio varied from 0.15 to 15.7. The average  $C_1/C_2$  ratio was higher in summer than that in winter comparing with different seasons and being consistent with the findings in Rome, Italy (Possanzini et al., 1996), eastern Finland (Viskari et al., 2000), and Kaohsiung, Taiwan (Wang et al., 2010). The higher ratio in summer may be related to the fact that the lifetime of formaldehyde exceeds acetaldehyde lifetime with respect to photolysis and different reactions with hydroxyl radicals (OH),  $NO_3$  radicals, and  $O_3$  (Atkinson, 2000). The reaction with OH radicals is often the dominant loss process for many carbonyls in photochemical polluted air. The calculated lifetimes due to reactions with OH radical are 1.2 day and 8.8 h for  $C_1$  and  $C_2$ , respectively (Atkinson, 2000). The  $C_1/C_2$  ratio is expected to be higher if loss process such as reaction with OH radicals dominates in summer. Higher  $C_1/C_2$  in summer also implies photo-oxidation of active hydrocarbons in which yields more formaldehyde than acetaldehyde (Duane et al., 2002; Guo et al., 2009). The highest  $C_1/C_2$  ratio was recorded in QH in both seasons whereas the lowest ratio was recorded in YT in winter and WH in summer. The average  $C_1/C_2$  ratios are  $\leq 2$  for urban areas in winter in which are close to previous measurements in urban areas in Beijing, Guangzhou, and Hong Kong (Feng et al., 2005; Ho et al., 2002). Low  $C_1/C_2$  ratios observed in WH and YT are mainly driven by high acetaldehyde emission from E-gasoline being used in these areas. Our results therefore suggest that the anthropogenic activities remain the dominant sources in both urban and sub-urban locations in China during winter.

The molar ratio of propionaldehyde to nonaldehyde ( $C_3/C_9$ ) is used as an indicator to determine the impact of vegetation emission. Propionaldehyde can be associated with anthropogenic emissions (Anderson et al., 1996), and thus the  $C_3/C_9$  ratio is typically found to be low in rural area. The  $C_3/C_9$  ratios showed large variations and the ratios in summer were lower than those in winter. This may reflect strong vegetation emission in summer. Despite the fact that the lifetime of nonaldehyde is shorter than propionaldehyde lifetime with respect to photolysis and reactions with OH radical, nitrate radical ( $NO_3$ ), and ozone (Atkinson, 2000), the high vegetation emission of nonaldehyde at high temperature may offset the loss due to photolysis and photochemical reactions. The lowest  $C_3/C_9$  ratio was recorded in QH in both seasons while the highest ratio was recorded in WH in winter and GZ in summer. Low  $C_3/C_9$  ratios observed in QH were due to high vegetation emission from this rural area.

### 3.4. Risk assessment

Inhalation is a major pathway for intake of carbonyls by human compared with ingestion and dermal absorption. Potential health risks for the two most abundant carbonyl compounds (formaldehyde and acetaldehyde) in nine cities are examined considering their carcinogenicity classified by U.S. Environmental Protection Agency (USEPA, 1998). Inhalation exposure is related to exposure frequency, duration, and activity pattern. These are essential factors in calculation of lifetime cancer hazard risk. Few assumptions assigned by U.S. EPA have been taken into account in relative carcinogenic assessment. The volume of air inhaled by a human is of  $20 \text{ m}^3 \text{ day}^{-1}$  and average body weight of 70 kg and these two assumptions are applied throughout the assessment. The inhalation unit risk estimate is  $1.3 \times 10^{-5} (\mu\text{g m}^{-3})^{-1}$  for formaldehyde

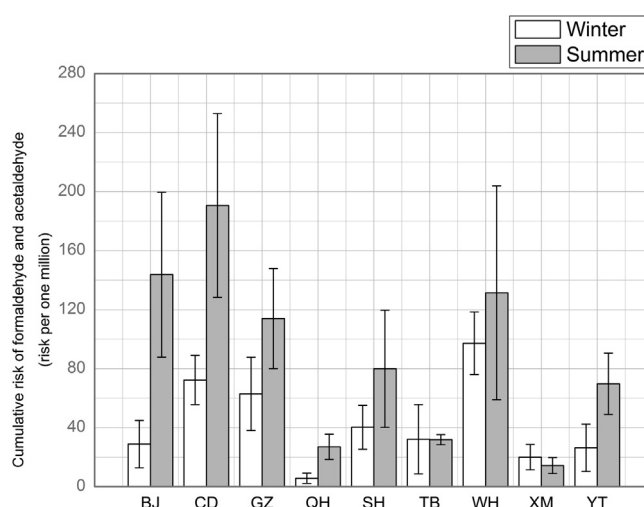


Fig. 2. Cumulative risks of formaldehyde and acetaldehyde among nine cities.

(USEPA, 1991b) and  $2.2 \times 10^{-6} (\mu\text{g m}^{-3})^{-1}$  for acetaldehyde (USEPA, 1991a). Risk below one in a million ( $<1 \times 10^{-6}$ ) is usually considered to be under concern level whereas the risk above 100 in a million ( $>1 \times 10^{-4}$ ) represents that instant actions or interventions are required to protect human health (Lee et al., 2006). The results are shown in Fig. 2. Higher cumulative cancer risks in general are observed in summer at all cities except XM. Chengdu (CD) demonstrates the highest cumulative risk in summer, followed by Beijing (BJ) and Wuhan (WH), however in winter the highest risk was in WH followed by CD. The lifetime cancer hazard risks associated with formaldehyde and acetaldehyde in WH are  $7.92 \times 10^{-5}$  and  $1.80 \times 10^{-5}$  in winter and  $1.17 \times 10^{-4}$  and  $1.49 \times 10^{-5}$  (WH) in summer. The same risks for YT are  $2.06 \times 10^{-5}$  and  $5.81 \times 10^{-6}$  (YT) in winter and  $6.20 \times 10^{-5}$  and  $7.79 \times 10^{-6}$  (YT) in summer. The high contribution of cancer risks from acetaldehyde observed in WH (winter: 18%; summer: 11%) and YT (winter: 22%; summer: 11%) can be attributed to the higher acetaldehyde emission from the E-gasoline.

## 4. Conclusion

The nationwide studies provide an overview of monocarbonyls concentrations in nine cities. Both photochemical reaction and vegetation emission are the major contributors in determining the carbonyl levels in summer while in winter the anthropogenic sources are the dominant contributors. In this study, the use of E-gasoline in certain cities lead to enhanced ambient levels of acetaldehyde that is classed as potentially carcinogenic compound. The results suggest that appropriate and effective pollution control strategy for carbonyls should be established in China particularly at the economically developing cities.

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