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Publisher: Taylor & Francis

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## Journal of the Air & Waste Management Association

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/uawm20>

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Accepted author version posted online: 14 Dec 2011. Version of record first published: 31 Jan 2012.

To cite this article: Steven Sai Hang Ho, Kin Fai Ho, Shun Cheng Lee, Yan Cheng, Jian Zhen Yu, Ka Man Lam, Natale Sin Yau Feng & Yu Huang (2012): Carbonyl emissions from vehicular exhausts sources in Hong Kong, *Journal of the Air & Waste Management Association*, 62:2, 221-234

To link to this article: <http://dx.doi.org/10.1080/10473289.2011.642952>

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# Carbonyl emissions from vehicular exhausts sources in Hong Kong

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*Vehicular emission (VE) is one of the important anthropogenic sources for airborne carbonyls in urban area. Six types of VE-dominated samples were collected at representative locations in Hong Kong where polluted by a particular fueled type of vehicles, including (i) a gas refilling taxis station (liquefied petroleum gas [LPG] emission); (ii) a light-duty passenger car park (gasoline emission); (iii) a minibus station (diesel emission); (iv) a single-deck-bus depot (diesel emission); (v) a double-deck-bus depot (diesel emission); and (vi) a whole-food market entrance for light- and heavy-duty vehicles (diesel emission). A total of 15 carbonyls in the samples were quantified. Formaldehyde was the most abundant carbonyl among the VE-dominated samples, and its contribution to the total quantified amount on a molar basis ranged from 54.8% to 60.8%. Acetaldehyde and acetone were the next two abundant carbonyls. The carbonyls were quantified at three roadside locations in Hong Kong. The highest concentrations of formaldehyde and acetaldehyde,  $22.7 \pm 8.4$  and  $6.0 \pm 2.8 \mu\text{g}/\text{m}^3$ , respectively, were determined in the samples collected at a main transportation gate for goods between Hong Kong and Mainland China. The total quantified carbonyl concentration,  $37.9 \pm 9.3 \mu\text{g}/\text{m}^3$ , was the highest at an entrance of a cross-harbor tunnel in downtown area. The theoretical carbonyls compositions of the three roadside locations were estimated according to the VE-dominated sample profiles and the statistics on vehicle numbers and types during the sampling period. The measured compositions of formaldehyde were much higher than the theoretical compositions in summer, demonstrating that photochemical reactions significantly contributed to the formaldehyde production in the roadsides.*

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## Introduction

Carbonyl (aldehyde and ketone) is an important group of airborne organic compounds in atmospheric chemistry. They photochemically dissociate to produce free radicals, which consequently initiate atmospheric reactions such as ozone formations at ground level (Atkinson et al., 1992; Carlier et al., 1986; Seinfeld and Pandis, 1998). Carbonyls are also important intermediates in the formation of photochemical smog (Birks, 1998). Besides, some carbonyls (e.g., formaldehyde, acetaldehyde, and acrolein) are known to be carcinogenic (World Health Organization (WHO), 2000). Their ambient levels are thus continuously monitored in Hong Kong and Mainland China.

Carbonyls can be either emitted into or formed in the atmosphere. Primary emission sources include both natural (e.g., biomass burning) and anthropogenic sources (e.g., automobile exhaust, cooking emission, incense burning, and cigarette smoke) (Grosjean et al., 1993; Ho and Yu, 2002; Ho et al., 2006; Risner, 1995; Villanueva-Fierro et al., 2004). Vehicular emission (VE) is one of the most important direct emission source of

anthropogenic origin in outdoor environments (Grosjean et al., 1993; Westerholm et al., 1991). A large number of studies have monitored gas- and/or particle-phase pollutant compositions in the vehicular exhausts. The gasoline- and diesel-fueled vehicle emissions are particularly important owing to their heavy daily usages in most developed and developing countries. Fuel reformation, use of lubricating oils, exhaust aftertreatment, and engine operation conditions can highly affect the compositions and volatilities of the pollutants emitted into the atmosphere (Ålander et al., 2005; Ålander et al., 2004; Westerholm and Egeback, 1994). Subchronic inhalation studies have also been conducted to investigate the toxicology in exposure of the atmospheres influenced by vehicular exhausts (McDonald et al., 2004; Liu et al., 2009). Apart from gasoline and diesel, other new power sources used as a fuel for vehicles have been studied as well. Corrêa and Arbilla (Corrêa and Arbilla, 2005) found that increase of formaldehyde levels is related to the use of compressed natural gas by the vehicular fleet, in substitution of gasohol (a mixture of gasoline and ethanol) in Brazil. Since the 1980s, a number of significant developments have been proposed and made in engine technology, aiming to

reduce the toxic pollutant levels in the exhausts (Hammerle et al., 1994). However, VE is now still the most significant pollution source in urban areas.

VE contributions to ambient volatile organic compounds (VOCs) have been widely studied. Their emission factors are typically derived from measurements of pollutant concentrations in roadway tunnels (Fraser et al., 1998; Kirchstetter et al., 1996; Kirchstetter et al., 1999b; Kirchstetter et al., 1999a; Lonneman et al., 1986). In previous studies, we have determined the emission factors for both VOCs and carbonyls at a roadway tunnel in Hong Kong (Ho et al., 2007, Ho et al., 2009). Influences from VE to the local ambient carbonyls in roadside environments had not been thoroughly investigated. In this study, each type of VE-dominated samples was collected in the atmosphere at a location (e.g., taxi station and bus depots), where is mainly contributed by a particular emission from vehicles fueled with liquefied petroleum gas (LPG), gasoline, or diesel. The chemical concentrations and profiles of the VE-dominated samples were compared and used to interpret their impacts on three local roadside locations. The significances of other anthropogenic and biogenic sources and photochemical reactions affecting the carbonyl compositions in the roadside airs are demonstrated. The findings can assist us to understand the contribution of VE to the ambient air in Hong Kong.

## Experimental Section

### Sampling sites

Sample collection can be divided into three different categories: VE-dominated, roadside, and background samples.

Figure 1 shows the locations of all sampling sites selected in this study.

VE-dominated samples: Ground-based roadside sampling at six traffic intersections and highway on/off ramps was conducted to obtain carbonyl source profiles for six categories of vehicles. The most important use of VE-dominated profiles is for the source marker identification for the different types of vehicular exhaust. The six sampling sites are described as below. (i) Wan Chai LPG refilling station (TAS) is located at Wan Shing Street, Wan Chai. The sampling equipment was placed at the roadside near the LPG refilling station. It was chosen to represent the LPG-fueled taxi emission. (ii) The Hong Kong Polytechnic University (HKPU) car park (PCX) is situated at ground floor of the HKPU, Hung Hom. The sampling equipment was placed at the entrance of the car park. It was chosen to represent the gasoline-fueled light-duty passenger car emissions. (iii) Shau Kei Wan minibus station (MBS) is situated at Mong Lung Street, Shau Kei Wan. The sampling equipment was placed next to the minibus station. It was chosen to represent the diesel-fueled minibus emission. (iv) The Peak Station (SBS) is situated at the Peak bus depot, near the Peak Road. The sampling equipment was placed at the roadside of the bus depot. It was chosen to represent the single-deck bus diesel emission. (v) Tuen Mun Bus Depot station (DBS) is located at the Ho Tin Street, Tuen Mun. The sampling equipment was placed at the roadside of the bus depot. It was chosen to represent the double-deck bus diesel emission. (vi) Cheung Sha Wan Whole Food Market station (GVX) is located at the Yen Chow Street West, Cheung Sha Wan. The sampling equipment was placed at the entrance of the whole-food market. It was chosen to represent the light- and heavy-duty vehicle diesel emission.

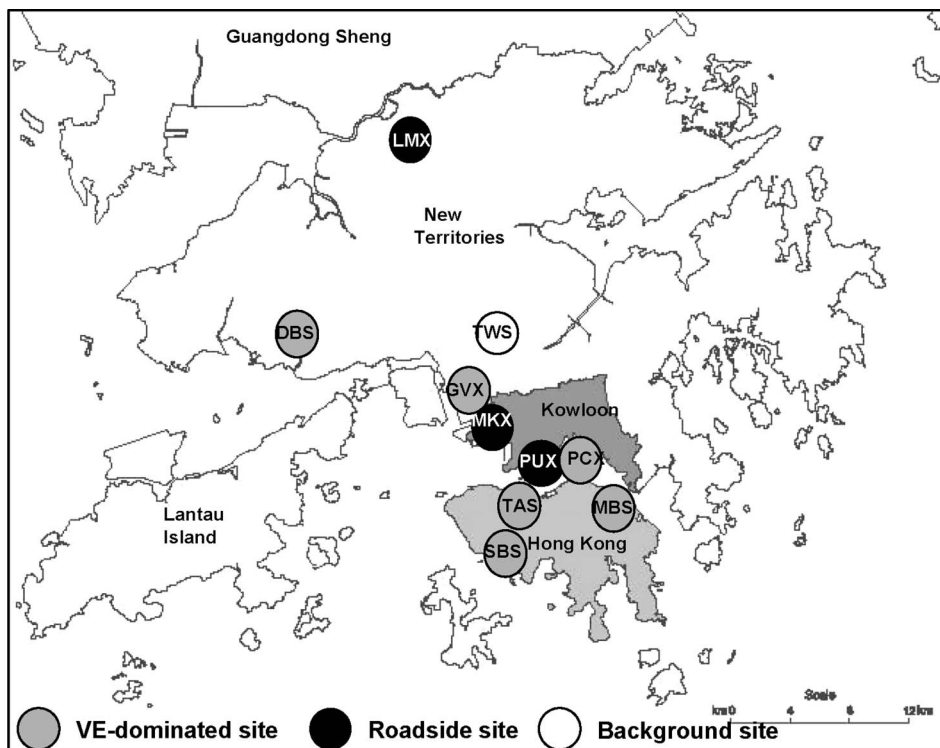


Figure 1. The map showing the sampling locations in this study. Location acronyms are shown in Table 1.

Roadside samples: (i) Mong Kok Hong Kong Environmental Protection Department (HKEPD) roadside air quality monitoring station (MKX) is located at the junction of the heavily traffic Lai Chi Kok Road and Nathan Road. (ii) HKPU roadside monitoring station (PUX) is located 1 m adjacent to Hong Chong Road, which links to the Cross Harbor Tunnel. Samples taken at these two roadside locations can represent street-level emissions from nearby vehicle exhaust and road dust. It is aimed to obtain slow traffic emission exhausts for cross-bounder vehicles. (iii) Lok Ma Chau roadside monitoring station (LMX) is located at the entrance of the boundary-crossing point where vehicles come from Mainland China to Hong Kong.

Air samples were also collected at Tsuen Wan HKEPD air quality monitoring station (TWS). It is located at the rooftop of the Princess Alexandra Community Centre, Tsuen Wan. It was chosen to represent the background ambient air in Hong Kong during the sampling period.

### Engine and fuel types

There were a large number of pre-Euro diesel-fueled buses and heavy-duty vehicles on the road in Hong Kong. In 2003, the pre-Euro fleet contributed >40% of the total number of heavy-duty vehicles and >10% of the buses. And Euro II fleet also had a contribution of >24% for heavy-duty vehicles and >30% for the buses. Compared with Euro IV vehicles (available in September, 2006), Euro II models emit seven times more respirable suspended particulates (RSP) and twice as much nitrogen oxides (NO<sub>x</sub>) (Hong Kong Government, 2010). Significant reductions in emissions could be achieved by replacing the Euro II or older diesel-fueled buses and heavy-duty vehicles with modern gas vehicles. However, nearly

identical reductions could be achieved by replacement with Euro V diesels (available in October, 2007) except NO<sub>x</sub> (Hong Kong Environmental Protection Department, 2005). In this study, classification of the diesel-fueled engine type by the Standard was not done owing to too many vehicles passing the monitoring stations in a short period. For the same reason, classification of gasoline vehicles by either models or years was not applicable as well. Therefore the intervariations of engines for each fueled type were not taken into account. Euro III unleaded petrol was the major fuel used in Hong Kong in 2003. Compared with the Euro IV unleaded petrol specifications (available in January, 2005), the Euro III unleaded petrol produces more sulfur by 67% and aromatic hydrocarbons by 17% (Hong Kong Government, 2004). It should be noted that a few heavy-duty vehicles might refill petrol in Mainland China during their journeys for goods transportation to Hong Kong. Its fuel specification might be thus varied from the Euro III standard.

### Sample collection

A total of 17 VE-dominated, 58 roadside, and 20 background samples, were collected in summer and winter of 2003. A minimum of three valid samples were obtained at each sampling location. Air samples were collected into silica cartridges impregnated with acidified 2,4-dinitrophenylhydrazine (DNPH) (Sep-Pak DNPH-silica, 55–105 μm particle size, 125Å pore size; Waters Corporation, Milford, MA) at a flow rate of 0.8–0.9 L/min for 2 hr (VE-dominated samples) or 3 hr (roadside and background samples) (Table 1). The samples for each VE-dominated source were collected when a maximum number of vehicles passed the sites. For the roadside samples,

**Table 1.** A summary of sampling site information

Location Acronym	Sampling Station	Vehicle Fueled Type	Sampling Session	Potential Influence Primary Sources <sup>a</sup>
Vehicular emission dominated sources				
TAS	Wan Chai LPG refilling station	LPG-fueled taxi emission	Afternoon	Residential and Commercial
PCX	The Hong Kong Polytechnic University car park	Gasoline-fueled light-duty passenger car emission	Afternoon	Nil
MBS	Shau Kei Wan minibus station	Diesel-fueled minibus emission	Morning	Residential
SBS	The Peak Station	Single-deck bus diesel emission	Morning	Residential
DBS	Tuen Mun Bus Depot station	Double-deck bus diesel emission	Afternoon	Residential
GVX	Cheung Sha Wan Whole Food Market station	Light- and heavy-duty vehicle diesel emission	Morning	Nil
Roadside locations				
MKX	Mong Kok Hong Kong Environmental Protection Department monitoring station	Mixed vehicle types	Afternoon	Residential and commercial
PUX	The Hong Kong Polytechnic University roadside monitoring station	Mixed vehicle types	Afternoon	Nil
LMX	Lok Ma Chau roadside monitoring station	Mainly diesel-fueled heavy-duty vehicles	Afternoon	Nil

Note: <sup>a</sup>Biogenic emission and photochemical reactions are excluded.

the collections were carried out during rush hours (slow traffic) but no traffic jam was observed. This avoids different carbonyls emission ratios from the idle engines. The background samples were collected in the daytime, consistent with the sampling periods for both of the VE-dominated and roadside samples. It is important to note that the carbonyls levels and compositions at the sites were possibly affected by other local emission sources, regional transportation of pollutants, and photochemical reactions of organic compounds in the atmosphere, even though the most representative sampling periods were chosen. Table 1 summarizes the potential primary sources contributed to each of the monitoring sites.

No breakthrough was found at such sampling flow rates and sampling times. The sampler was fixed on the ground level with an inlet at a height of ~1.5 m (breathing zone). The flow rates were checked in the field in the beginning and at the end of each sampling using a calibrated flow meter. An ozone scrubber (Waters) was installed in front of the DNPH-silica cartridge in order to prevent possible influence of ozone. The DNPH cartridges were stored in a refrigerator at <4 °C after sampling and before analysis.

### Sample analysis

Chemical analysis was carried out at the Hong Kong University of Science and Technology (HKUST). Each DNPH cartridge was eluted with 2.0 mL of acetone-free acetonitrile (high-performance liquid chromatography/gas chromatography [HPLC/GC] grade; Mallinckrodt Laboratory Chemicals, Phillipsburg, NJ) to a volumetric flask. Test has been done to demonstrate that no any DNPH and its derivatives remained in the cartridge after the 2-mL elution (Ho et al., 2007). Certified calibration standards of the DNPH-carbonyl derivatives were purchased from Supelco (Bellefonte, PA) and diluted into concentration ranges of 0.05–5.0 mg/mL for formaldehyde and 0.05–2.0 mg/mL for the other carbonyls. Linearity was indicated by a correlation of determination ( $r^2$ ) of at least 0.999. The samples and standards were analyzed by injecting 20  $\mu$ L of the solutions to an Hewlett Packard gradient HPLC 1100 system (Santa Clara, CA) equipped with a photodiode array detector (DAD). The column for separation was a  $4.6 \times 150$ -mm Hypersil ODS 5-mm reversed phase column (Alltech, Deerfield, IL) at room temperature. The mobile phase consisted of two solvent mixtures: mixture A, 60:30:10 (v/v) of water/acetonitrile/tetrahydrofuran; mixture B, 40:60 (v/v) of water/acetonitrile. The gradient program was 100% A for 1 min, followed by a linear gradient from 100% A to 100% B in 10 min. The flow rate was 1.5 mL/min for the first 15 min, increased to 1.7 mL/min in 2 min, and maintained at this flow until the end of the analysis. Absorbance at 360 nm was used for quantification of the DNPH-carbonyl derivatives. The limit of detection (LOD) was done by analyzing a minimum of seven replicates of a standard solution containing the analytes at a concentration of 0.02 mg/mL. It is estimated using the equation:

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

where  $t_{(n-1, 1-\alpha=99\%)}$  is the student's  $t$ -distribution value at  $n - 1$  degrees of freedom, and  $S$  is the standard derivation of

the replicates. The LODs of the target carbonyls ranged from 0.002 to 0.010 mg/mL, which can be translated into 0.05–0.12  $\mu\text{g}/\text{m}^3$  for the sampling volumes.

## Results and Discussion

### Background carbonyl concentrations

Table 2 shows the concentrations of 15 carbonyls in TWS during the sampling periods in 2003. This site represents the background concentrations of urban area in Hong Kong. Both anthropogenic emissions and photochemical reactions can contribute to the carbonyl formations. Unsaturated carbonyls including acrolein and crotonaldehyde were detected but their abundances were not reported in the study. The unstable carbonyl DNP-hydrazone can react with excess reagent to form adducts, which could not be accurately quantified due to chromatographic and response factor issues (Schulte-Ladbeck et al., 2003, Ho et al., 2011). Formaldehyde, acetaldehyde, and acetone were the three most abundant carbonyls, with an average of  $8.7 \pm 3.0$ ,  $4.9 \pm 1.7$ , and  $2.4 \pm 3.0 \mu\text{g}/\text{m}^3$ , respectively. The ambient levels were within the ranges measured at the same sampling site between 1997 and 2000 (Sin et al., 2001)

### Vehicular-emission-dominated samples

Concentrations of the carbonyls in the six types of VE-dominated samples are listed in Table 3. The absolute values are difficult to compare with the background concentrations because wind directions and air dilution rates varied among the monitoring sites. In addition, we must point out again that other anthropogenic emissions and photochemical reactions possibly affect the carbonyls concentrations and compositions in the VE-

**Table 2.** Carbonyls concentrations in background station of TWS

Site	TWS Tsuen Wan Carbonyls Concentrations ( $\mu\text{g}/\text{m}^3$ ) ( $n = 20$ )	
	Mean	SD
Background station		
Formaldehyde (C1)	8.7	3.0
Acetaldehyde (C2)	4.9	1.7
Acetone (C3K)	2.4	3.1
Propionaldehyde (nC3)	0.56	0.20
Methyl ethyl ketone (MEK)	0.61	0.27
<i>i</i> - <i>n</i> -butyraldehyde ( <i>i</i> /nC4)	0.79	0.35
Benzaldehyde (benz)	1.0	0.38
<i>iso</i> -Valeraldehyde ( <i>i</i> C5)	1.0	0.36
<i>n</i> -Valeraldehyde (nC5)	0.75	0.55
<i>o</i> -Tolualdehyde ( <i>o</i> -tol)	0.04	0.07
<i>m,p</i> -tolualdehyde ( <i>m/p</i> -tol)	0.17	0.15
<i>n</i> -Hexaldehyde (C6)	0.39	0.16
2,5-Dimethylbenzaldehyde (2,5-DB)	0.11	0.07
Total	21.5	6.9

**Table 3.** Carbonyls concentrations in different types of vehicular-emission-dominated samples

Site	TAS		PCX		MBS		SBS		DBS		GVX	
Vehicle type	Taxis		Light-duty passenger cars		Minibuses		Single-deck big buses		Double-deck big buses		Light- and heavy-duty vehicles	
Fuel type	LPG		Gasoline		Diesel		Diesel		Diesel		Diesel	
Carbonyls Concentrations ( $\mu\text{g}/\text{m}^3$ )												
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Formaldehyde	11.1	3.8	7.5	0.64	22.0	7.2	9.0	0.33	5.3	3.1	17.2	1.9
Acetaldehyde	6.4	2.5	3.6	0.55	8.5	2.3	3.6	0.75	2.4	1.7	8.7	0.69
Acetone	3.8	0.76	2.0	1.3	8.7	1.7	3.8	0.37	1.6	1.0	4.3	1.5
Propionaldehyde	0.60	0.49	0.07	0.06	1.0	0.70	0.27	0.17	0.41	0.13	0.85	0.35
Methyl ethyl ketone	0.78	0.61	0.64	0.25	1.3	0.59	1.1	0.11	0.52	0.11	2.3	0.29
<i>i/n</i> -Butyraldehyde	1.2	0.32	0.68	0.37	1.4	0.47	0.44	0.21	0.82	0.29	1.5	0.17
Benzaldehyde	1.7	1.1	0.65	0.57	2.4	0.92	0.74	0.11	0.69	0.12	1.6	0.27
<i>iso</i> -Valeraldehyde	1.6	0.78	0.64	0.41	2.2	0.21	1.8	1.0	0.67	0.21	1.5	0.70
<i>n</i> -Valeraldehyde	1.3	0.31	0.20	0.02	1.8	0.20	0.17	0.08	0.37	0.14	1.6	0.46
<i>o</i> -Tolualdehyde	0.09	0.02	0.40	0.28	1.0	0.21	0.05	0.08	0.27	0.06	0.34	0.02
<i>m,p</i> -Tolualdehyde	bd <sup>a</sup>	—	0.28	0.19	0.39	0.06	bd	—	0.11	0.07	0.15	0.09
<i>n</i> -Hexaldehyde	0.35	0.25	0.32	0.17	0.91	0.46	0.23	0.11	0.35	0.13	0.66	0.10
2,5-Dimethylbenzaldehyde	0.11	0.08	0.09	0.06	0.63	0.45	bd	—	0.23	0.01	0.43	0.13
Total	29.0	9.9	17.0	5.1	52.3	11.8	21.1	1.7	13.8	4.4	41.1	3.3

Note: <sup>a</sup>“bd” represents below limit of detection (LOD)

dominated samples collected in the real environments. To our best effort, these uncertainties have been minimized by selection of the most representative sampling periods and locations and collections of the samples under similar meteorological conditions. According to the Registration and Licensing of Vehicles by Fuel Type in March, 2004, released by Hong Kong Transport Department (2004), 99% of taxis were LPG-fueled; 99% of motorcycles and light-duty messenger cars were gasoline-fueled; and 80% of minibuses, 95% of light-duty vehicles, and 100% of big buses (including single- and double-deck) and heavy-duty vehicles were diesel-fueled. Our source samples are classified using this guideline. The highest total quantified carbonyls concentration,  $52.3 \pm 11.8 \mu\text{g}/\text{m}^3$  on average, was found at the diesel-fueled minibus station (MBS). The mean total concentrations were  $21.1 \pm 1.7$  and  $13.8 \pm 4.4 \mu\text{g}/\text{m}^3$ , respectively, at the diesel-fueled single-deck-bus (SBS) and double-deck-bus (DBS) depots. The diesel-fueled heavy-duty VE-dominated samples were collected in GVX, which had a mean concentration of  $41.1 \pm 3.3 \mu\text{g}/\text{m}^3$ . The total quantified carbonyls concentration was  $29.0 \pm 9.9 \mu\text{g}/\text{m}^3$  on average at the LPG-fueled taxi station (TAS), whereas a lower value of  $17.0 \pm 5.1 \mu\text{g}/\text{m}^3$  was found in the gasoline-fueled light-duty passenger cars VE-dominated samples (PCX).

Formaldehyde was the most abundant carbonyl, which ranged from 5.3 to 22.0  $\mu\text{g}/\text{m}^3$  among the VE-dominated samples. It accounted for 54.9% to 60.8% to the total quantified carbonyls. The contributions were very close to the average value of the TWS samples (57.2%), indicating that the VE was also the major pollution source for the background site. Acetaldehyde and acetone were the next two abundant carbonyls, ranging from 2.4

to 8.7  $\mu\text{g}/\text{m}^3$  and 1.6 to 8.7  $\mu\text{g}/\text{m}^3$ , respectively, and their contributions varied from 15.7% to 21.6% and 7.6% to 12.9%, respectively. Other carbonyls had minor concentrations of  $<2.5 \mu\text{g}/\text{m}^3$ , which accounted for  $<17\%$  to the total quantified carbonyls.

Carbonyl molar composition profiles in the different types of VE-dominated samples are shown in Figure 2. The LPG-fueled VE-dominated samples had the lowest contributions of formaldehyde (54.9%), *o*-tolualdehyde (0.1%) and *m/p*-tolualdehyde (below LOD) and the highest contributions of acetaldehyde (21.6%), benzaldehyde (2.4%), and *n*-valeraldehyde (2.3%). Propane, *n*-butane, and *i*-butane are the major constituents of LPG in Hong Kong (Tsai et al., 2006). However, the total C<sub>3</sub> (acetone and propionaldehyde) and C<sub>4</sub> (*i/n*-butyraldehyde and MEK) carbonyls contribution (15.4%) is similar to the average of 15.8% in the other VE-dominated samples. For the gasoline-fueled VE-dominated samples, the lowest contribution of propionaldehyde (0.3%) was seen but the contributions of total tolualdehyde isomers (1.4%) were the highest among all the VE-dominated samples.

The carbonyls profiles were different along the diesel-fueled VE-dominated samples. Acetaldehyde and MEK had the lowest contributions in the minibus VE-dominated samples, which accounted for 15.7% and 1.5%, respectively, to the total quantified carbonyls. Acetone and *iso*-valeraldehyde had the highest contributions, 12.9% and 4.1%, respectively, in the single-deck VE-dominated samples, whereas the contributions of other carbonyls ( $\geq\text{C}_4$ ) were the lowest. The highest contributions of heavier carbonyls such as *n*-hexaldehyde and 2,5-dimethylbenzaldehyde together with propionaldehyde and *i/n*-butyraldehyde were seen in the double-deck VE-dominated

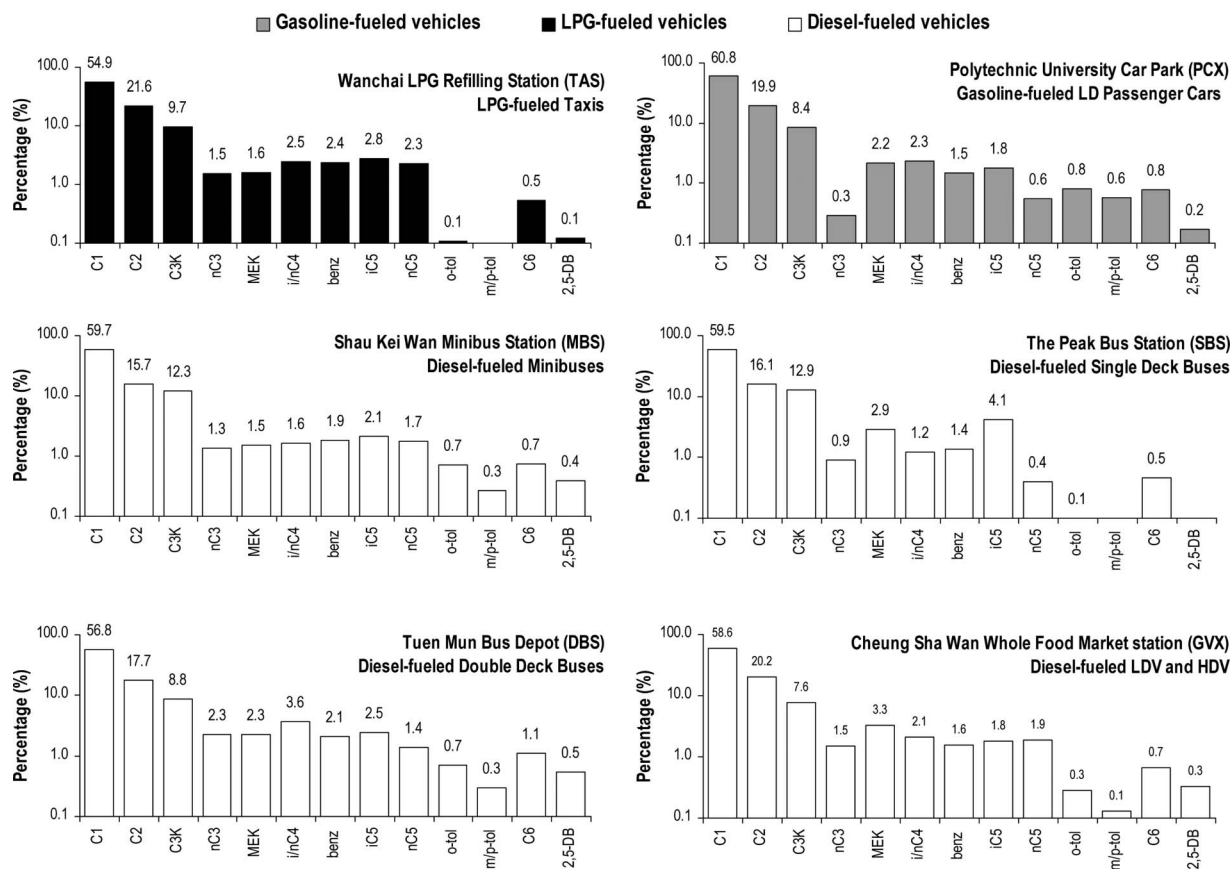


Figure 2. Average carbonyls molar composition profiles for the six VE-dominated samples. Carbonyl acronyms are shown in Table 2.

samples. The highest contribution of MEK was found in the heavy-duty VE-dominated samples, which accounted for 3.3% to the total quantified carbonyls. The variation of engines equipped in the diesel-fueled vehicles is a possible explanation for the different carbonyl compositions.

It is important to illustrate that tolualdehydes are characteristics of the gasoline and the diesel VE because of the absences of *m*-/*p*-tolualdehyde and very trace contribution of *o*-tolualdehyde in the LPG VE-dominated samples. Xylene isomers (including *o*-, *m*-, and *p*-) are constituents of gasoline that can be emitted into the atmosphere, either from fugitive emissions of gasoline or gasoline-fueled vehicle exhaust (Fraser et al., 1998, Kirchstetter et al., 1996, Olson et al., 1992, Zielinska et al., 1996). They can react with hydroxyl (OH) or nitrate (NO<sub>3</sub>) radicals to form hydroxydimethylcyclohexadienyl and methylbenzyl radicals that leads the formation of *o*-, *m*-, or *p*-tolualdehyde (Atkinson, 1994; 2000; Calvert et al., 2002).

### Carbonyls in roadside locations

Table 4 shows the carbonyls concentrations and their contributions to the total quantified species collected in the atmosphere at different roadside locations in Hong Kong. The vehicle numbers and their fuel types were counted during sampling events in order to evaluate their effects on the ambient concentrations. The statistical counting precision were <1%.

The total quantified carbonyls at the three roadside locations, ranging from  $31.1 \pm 10.7$  to  $37.9 \pm 9.5 \mu\text{g}/\text{m}^3$ , were significantly higher than the value of  $21.5 \pm 6.9 \mu\text{g}/\text{m}^3$  measured in background site of TWS. This demonstrates the strong contribution of VE to the carbonyl levels in the roadsides. The highest ambient concentrations of formaldehyde and acetaldehyde were determined in the samples collected in LMX, with an average of  $22.7 \pm 8.4$  and  $6.0 \pm 2.8 \mu\text{g}/\text{m}^3$ , respectively. The site is the main transportation gate for goods between Hong Kong and China. More than 80% of the vehicles passing through the site were diesel-fueled light- and heavy-duty vehicles during the sampling events. Apart from the local VE, the pollutants generated by biogenic and anthropogenic sources in Mainland China may transport to the atmosphere in the border area. The highest mean total quantified carbonyls concentration of  $37.9 \pm 9.3 \mu\text{g}/\text{m}^3$  was seen in the atmosphere in MKX. The downtown site is surrounded by tall residential and commercial buildings, resulting in poor air ventilation and pollutant dilution. Other anthropogenic emissions such as commercial cooking activities can also degrade the air quality in the downtown area (Ho et al., 2006). The ambient concentrations of *o*-tolualdehyde and *m*-/*p*-tolualdehyde were the highest in MKX as well, which had concentrations of  $0.16 \pm 0.16$  and  $0.44 \pm 0.28 \mu\text{g}/\text{m}^3$  on average, respectively. Even though the statistic shows that the amounts and contributions of gasoline-fueled light-duty passenger cars and motorcycles passing MKX were not higher than other sites, emissions from unrecorded vehicles on nearby roads and the

**Table 4.** Carbonyls concentrations and the traffic counts in three roadside locations in Hong Kong

Site Roadside location	LMX Lok Ma Chau ( <i>n</i> = 19)		MKX Mong Kok ( <i>n</i> = 19)		PUX HKPU ( <i>n</i> = 20)	
	Carbonyls Concentrations ( $\mu\text{g}/\text{m}^3$ )					
	Mean	SD	Mean	SD	Mean	SD
Formaldehyde	22.7	8.4	19.0	5.3	17.1	5.8
Acetaldehyde	6.0	2.8	5.7	1.6	5.1	1.8
Acetone	2.8	1.8	6.8	2.9	4.7	3.9
Propionaldehyde	0.90	0.49	0.79	0.32	0.59	0.26
Methyl ethyl ketone	0.52	0.52	1.0	0.51	0.77	0.66
<i>i</i> -/ <i>n</i> -Butyraldehyde	0.92	0.47	0.57	0.28	0.49	0.30
Benzaldehyde	0.53	0.33	0.83	0.34	0.73	0.42
<i>iso</i> -Valeraldehyde	0.83	0.43	1.4	0.76	0.61	0.43
<i>n</i> -Valeraldehyde	1.3	0.93	0.67	0.54	0.32	0.16
<i>o</i> -Tolualdehyde	0.06	0.09	0.16	0.16	0.07	0.08
<i>m,p</i> -Tolualdehyde	0.27	0.13	0.44	0.28	0.22	0.20
<i>n</i> -Hexaldehyde	0.56	0.27	0.74	0.29	0.54	0.11
2,5-Dimethylbenzaldehyde	0.22	0.32	0.19	0.25	0.14	0.22
Total	37.6	12.6	37.9	9.3	31.1	10.7

Number of Vehicle Classified by Vehicle Type							
	Fuel Type	Mean	SD	Mean	SD	Mean	SD
Taxi	LPG	0	0	631	148	2886	240
Motorcycles	Gasoline	2	2	97	36	568	112
LD passenger cars	Gasoline	492	132	736	229	4579	286
Minibuses	Diesel	30	30	547	101	318	203
Big buses	Diesel	149	59	171	228	888	388
LDV	Diesel	6	5	554	140	2190	506
HDV	Diesel	1791	362	273	84	1717	241
Total		2469	513	3009	662	13146	789

Number of Vehicle Classified by Fuel Type							
	Mean	SD	Mean	SD	Mean	SD	
LPG	0	0	631	148	2886	240	
Gasoline	494	131	833	261	5147	361	
Diesel	1975	398	1545	348	5113	553	
Total	2469	513	3009	662	13146	789	

accumulation of air pollutants could greatly affect the ambient levels of carbonyls. A high level of total quantified carbonyls was also found in PUX, with an average of  $31.1 \pm 10.7 \mu\text{g}/\text{m}^3$ . The site is at the tunnel exit in downtown area and its atmosphere is mainly polluted by the VE. The record shows an average of >5000 of different types of LPG-, gasoline-, and diesel-fueled vehicles passing the site during the sampling events.

A comparison of the carbonyls levels between this study and reports on other roadside locations is illustrated in Table 5. As expected, formaldehyde and acetaldehyde were the most two abundant carbonyls in the airs contributed by VE. Our findings are consistent with observation from Morknoy et al. (2011) that higher concentrations of formaldehyde and acetaldehyde were seen at the roadsides in Bangkok, whereas at least 10% lower in their concentrations were measured at the residential areas. Our

average concentrations of formaldehyde were slightly higher than that at other roadside locations in Hong Kong ( $6.4\text{--}16.7 \mu\text{g}/\text{m}^3$ ) (Ho et al., 2006) and Guiyang, China ( $18.0 \pm 6.5 \mu\text{g}/\text{m}^3$ ) (Ho et al., 2006) and Guiyang, China ( $9.4 \pm 3.2 \mu\text{g}/\text{m}^3$ ) (Pang and Lee, 2010). For acetaldehyde, the average concentrations in the three sites were within the ranges reported in the other roadside sites in Hong Kong ( $3.6\text{--}13.9 \mu\text{g}/\text{m}^3$ ) (Ho et al., 2006) and Guiyang, China ( $9.4 \pm 3.2 \mu\text{g}/\text{m}^3$ ) (Pang and Lee, 2010). On a worldwide basis, the formaldehyde concentrations in our samples were close to the values measured at roadside sites in Kolkata, India (Dutta et al., 2010), Ealing, United Kingdom (Williams et al., 1996), and Rio de Janeiro, Brazil (Corrêa and Arbilla, 2005). Larger variations in acetaldehyde concentrations were seen among the roadside locations. Our values were also within the ranges measured in other Asian and European cities



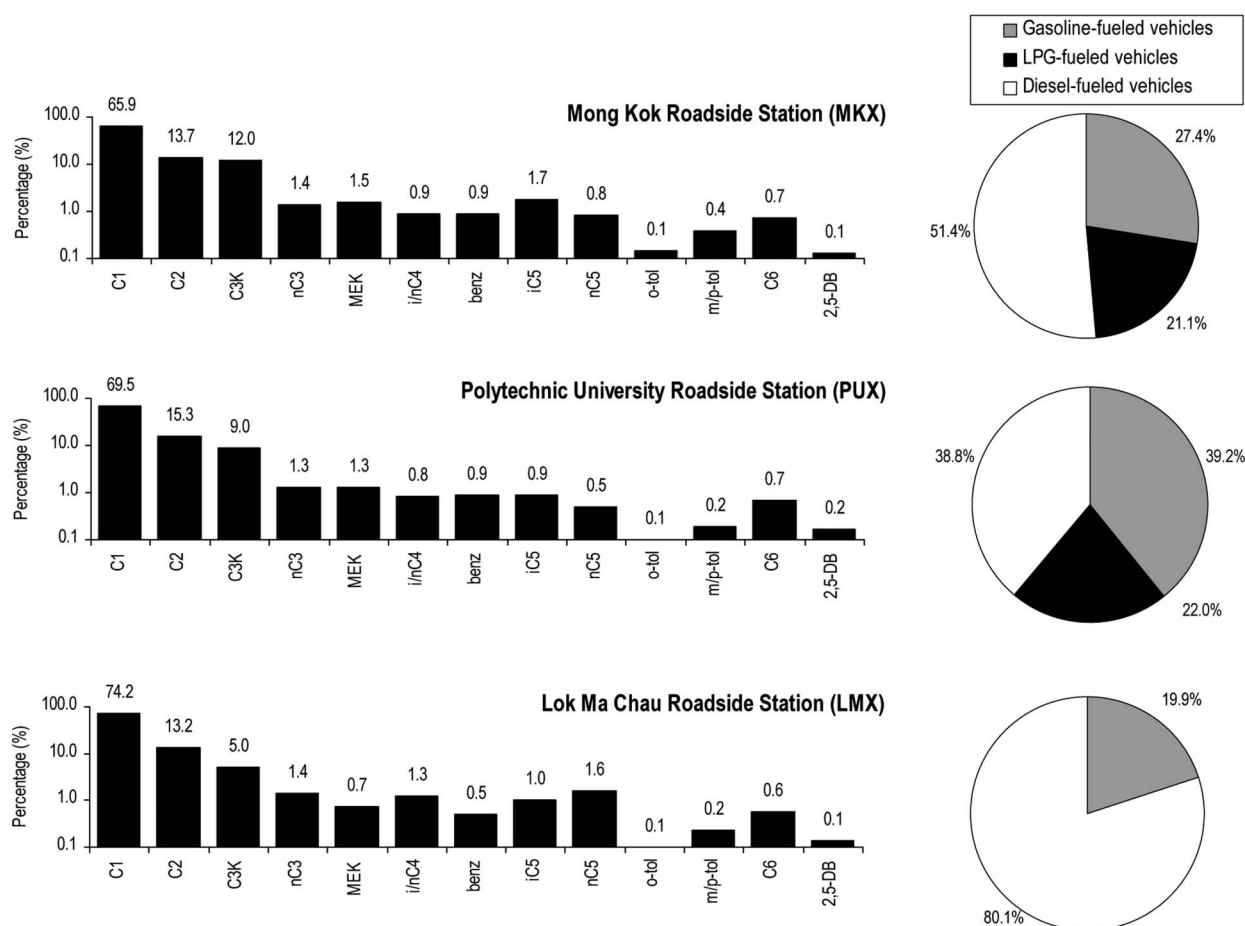
**Table 5.** Mean concentrations ( $\mu\text{g}/\text{m}^3$ ) of formaldehyde and acetaldehyde at roadside sites in other countries

Roadside Location	Sampling Period	Formaldehyde	Acetaldehyde	Reference
Lok Ma Chau, Hong Kong	Summer and winter 2003	$22.7 \pm 8.4$	$6.0 \pm 2.8$	This study
Mong Kok, Hong Kong	Summer and winter 2003	$19.0 \pm 5.3$	$5.7 \pm 1.6$	This study
HKPU, Hong Kong	Summer and winter 2003	$17.1 \pm 5.8$	$5.1 \pm 1.8$	This study
Central, Hong Kong	Summer and winter 2001	8.8	7.8–10.9	(Ho et al., 2006)
Chinese University, Hong Kong	Summer and winter 2001	5.6–9.1	7.2–9.2	(Ho et al., 2006)
Kwai Chung, Hong Kong	Summer and winter 2001	6.4–16.7	7.2–13.9	(Ho et al., 2006)
Shatin, Hong Kong	Summer and winter 2001	8.3–8.8	8.7–9.3	(Ho et al., 2006)
Guiyang, China	December 2008–August 2009	$18.0 \pm 6.5$	$9.4 \pm 3.2$	(Pang and Lee, 2010)
Bangkok, Thailand	July 2007–April 2008	5.14–17.2	3.06–19.9	(Morknoy et al., 2011)
Kolkata, India	November 2007–June 2008	8.55–23.64	9.29–17.49	(Dutta et al., 2010)
Ealing, United Kingdom	1991–1992	18.8–26.6	2.9–4.6	(Williams et al., 1996)
Wood Green, United Kingdom	1991–1992	4.9–9.2	3.5–4.3	(Williams et al., 1996)
Rio de Janeiro, Brazil	December 1998–January 2001	$18.3 \pm 21.1$	$26.3 \pm 25.6$	(Corrêa and Arbilla, 2005)

but were much lower than that in Rio de Janeiro, Brazil ( $26.3 \pm 25.6 \mu\text{g}/\text{m}^3$ ) (Corrêa and Arbilla, 2005). These demonstrate that variations of fuel specifications, engine types, and traffic numbers can affect greatly the carbonyl concentrations and compositions in the countries.

Carbonyl molar compositions in the roadside samples are shown in Figure 3. Formaldehyde was the most abundant

carbonyl, which accounted for 65.9% to 74.2% to the total quantified carbonyls. These values were much higher than its average contribution at the background site. Acetaldehyde and acetone are the next two abundant carbonyls. The contribution of acetaldehyde ranged from 13.2% to 22.0%. Our findings were consistent with the local carbonyls compositions reported by Ho and Lee (2002) and Ho et al. (2002), which the air samples were

**Figure 3.** Average carbonyls molar and vehicle fueled-type compositions at the three roadside stations.

collected at the cross-harbor tunnel entrance and the public transportation station. Greater variations in contributions for acetone were seen in the roadside samples, which ranged from 6.9% to 12.0%. Besides the three carbonyls, other carbonyls were also present but their contributions were all <3%. The highest contributions of *o*-tolualdehyde and *m*-*p*-tolualdehyde, 0.1% and 0.4% on average, respectively, were found in MKX. The result also promises an important input of gasoline-fueled VE to the downtown area.

### Seasonal variations of carbonyls at roadside locations

In Hong Kong, the period between May and August is classified as summer season, whereas the period between November and February is winter season (Lee et al., 2002). Table 6 compares the carbonyls concentrations in the roadside samples collected in summer and winter in 2003. The total quantified carbonyls concentrations were higher in the summer than that in winter. Formaldehyde had the same trend, which is consistent with previous roadside measurements in Hong Kong (Guo et al., 2004; Ho and Yu, 2002; Lee et al., 2001). No significant variation in the traffic counts was found between the two seasons in the three locations. The amounts of primary vehicular emissions sources were thus assumed to be similar. Formaldehyde can be emitted directly from engine exhaust or photochemically formed in the atmosphere from precursors (Althuller, 1993; Friedfeld

et al., 2002; Granby et al., 1997; Kawamura et al., 2000; Possanzini et al., 2002; Possanzini et al., 1996; Satsumabayashi et al., 1995). The secondary photochemical formation processes are also important sources for formaldehyde in summer. The seasonal variations of acetaldehyde and benzaldehyde are different from formaldehyde. Higher concentrations of these carbonyls were found in winter. We had the same observation on the data collected in the roadside locations in Hong Kong (Ho and Lee, 2002, Guo et al., 2004, Ho et al., 2002). The phenomenon can be explained by less photochemical reactions and more contributions from regional sources in winter. The decrease of acetone concentration in summer was obvious in LMX. It is reasonable because the photochemical processes consume but not produce acetone (Seinfeld, 1986). However, the decrease of acetone was not found in the downtown sites of MKX and PUX. More acetone might be produced by other anthropogenic emission sources such as cooking activities (Zhang and Smith, 1999). Minor carbonyls do not indicate consistent seasonal trends. Their concentrations could be influenced by different local and regional pollution sources. Meteorological parameters such as temperature, relative humidity, and wind direction can also affect the formations and sinks of the carbonyls in the atmosphere.

The theoretical carbonyls compositions of the three roadside locations were estimated according to the VE-dominated sample profiles and the statistics on vehicle numbers and types during

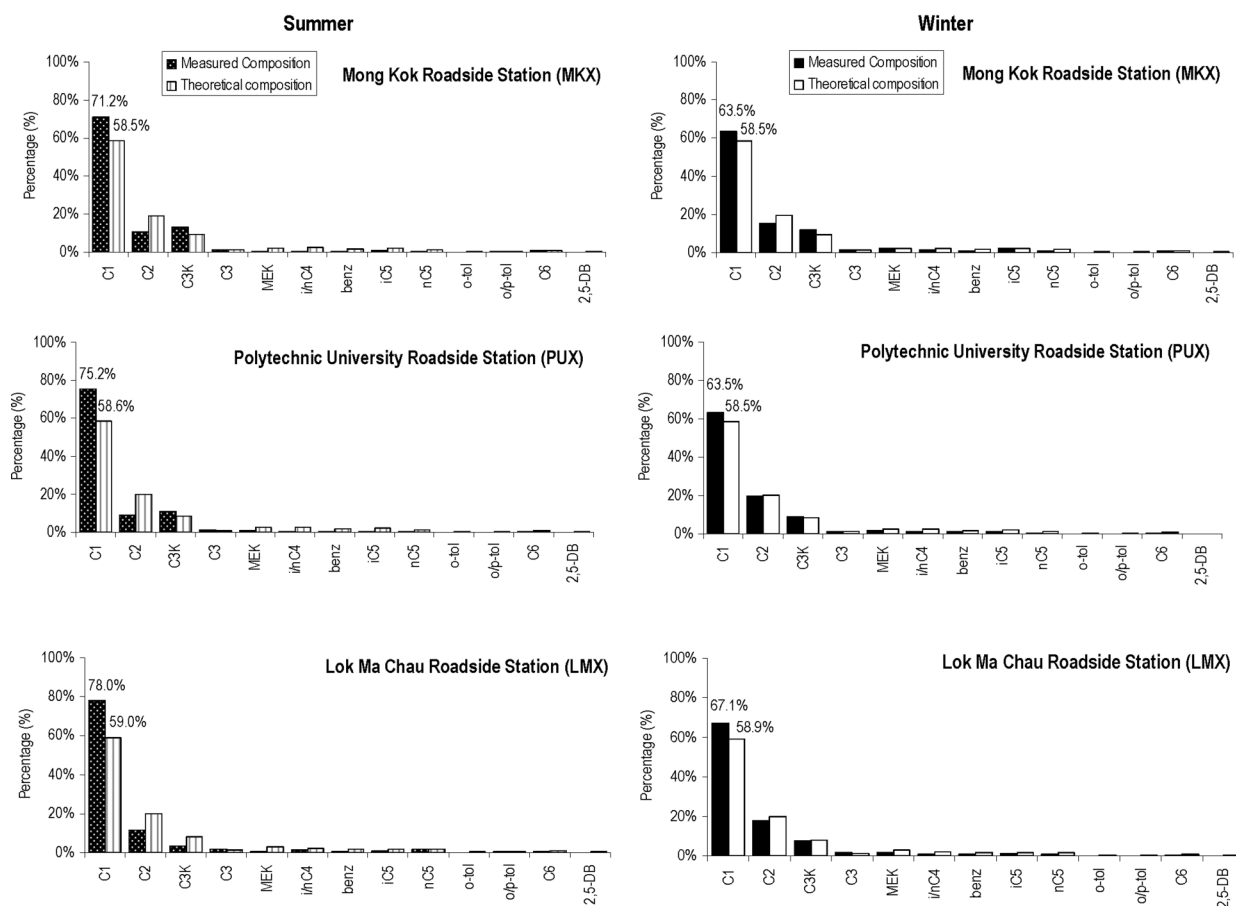


Figure 4. Comparison of measured and theoretical molar compositions at the three roadside stations in summer and winter.

Table 6. Seasonal variations of carbonyl concentrations and the traffic counts in three roadside locations in Hong Kong

Site	LMX		MKX		PUX	
	Lok Ma Chau		Mong Kok		HKPU	
Roadside location	Summer	Winter	Summer	Winter	Summer	Winter
	Mean	SD	Mean	SD	Mean	SD
Formaldehyde	25.2	8.6	18.5	7.1	23.7	4.7
Acetaldehyde	5.4	2.6	7.2	3.2	5.1	0.9
Acetone	2.1	1.6	4.0	1.9	8.5	2.1
Propionaldehyde	1.0	0.52	0.82	0.50	0.90	0.32
Methyl ethyl ketone	0.23	0.28	1.0	0.46	0.35	0.29
<i>i</i> - <i>n</i> -Butyraldehyde	1.1	0.35	0.65	0.57	0.28	0.28
Benzaldehyde	0.46	0.32	0.63	0.36	0.48	0.26
<i>iso</i> -Valeraldehyde	0.70	0.34	1.1	0.53	0.68	0.33
<i>n</i> -Valeraldehyde	1.7	0.94	0.59	0.19	0.60	0.40
<i>o</i> -Tolualdehyde	bd <sup>a</sup>	—	0.17	0.02	bd	—
<i>m,p</i> -Tolualdehyde	0.31	0.12	0.19	0.11	0.43	0.42
<i>n</i> -Hexaldehyde	0.68	0.24	0.36	0.20	1.0	0.26
2,5-Dimethylbenzaldehyde	0.24	0.37	0.16	0.06	bd	—
Total	39.0	13.4	35.2	12.4	41.9	6.5
C <sub>1</sub> /C <sub>2</sub> molar ratio	7.6	2.0	3.9	0.3	6.8	0.6
C <sub>2</sub> /C <sub>3</sub> molar ratio	7.7	1.0	12.8	3.4	8.0	2.3
	Mean	SD	Mean	SD	Mean	SD
Carbonyls Concentrations (µg/m <sup>3</sup> )	22.1	4.4	17.1	4.4	22.1	4.5
Formaldehyde	13.3	3.1	6.0	1.7	3.9	1.8
Acetaldehyde	6.1	1.1	6.2	3.0	6.2	4.4
Acetone	3.7	3.3	0.74	0.32	0.72	0.33
Propionaldehyde	0.49	0.17	1.3	0.29	0.70	0.67
Methyl ethyl ketone	0.83	0.70	0.69	0.19	0.35	0.29
<i>i</i> - <i>n</i> -Butyraldehyde	0.62	0.27	1.0	0.26	0.60	0.56
Benzaldehyde	0.83	0.28	1.6	0.71	0.38	0.23
<i>iso</i> -Valeraldehyde	0.81	0.47	0.70	0.60	0.28	0.20
<i>n</i> -Valeraldehyde	0.36	0.12	0.25	0.14	0.07	0.08
<i>o</i> -Tolualdehyde	bd	—	0.45	0.11	0.18	0.19
<i>m,p</i> -Tolualdehyde	0.44	0.05	0.64	0.26	0.60	0.11
<i>n</i> -Hexaldehyde	0.49	0.08	0.37	0.24	bd	—
2,5-Dimethylbenzaldehyde	0.42	0.12	36.3	10.0	36.1	12.0
Total	27.4	8.5	4.4	0.9	9.3	2.4
C <sub>1</sub> /C <sub>2</sub> molar ratio	3.2	0.4	11.1	2.4	7.3	1.4
C <sub>2</sub> /C <sub>3</sub> molar ratio	18.7	8.5	2823	616	13132	665

Fuel Type	Number of Vehicle Classified by Vehicle Type		Number of Vehicle Classified by Fuel Type	
	Mean	SD	Mean	SD
Taxis	0	0	596	124
Motorcycles	3	2	109	44
LD passenger cars	442	83	894	264
Minibuses	32	38	596	124
Big buses	123	54	515	56
LDV	8	4	520	96
HDV	1621	306	244	56
Total	2229	392	3474	600
	Mean <td>SD <td>Mean <td>SD </td></td></td>	SD <td>Mean <td>SD </td></td>	Mean <td>SD </td>	SD
LPG	0	0	645	160
Gasoline	3	2	92	33
Gasoline	442	83	673	193
Diesel	32	38	528	90
Diesel	123	54	34	21
Diesel	8	4	568	156
Diesel	1621	306	284	93
Total	2229	392	2823	616
	Mean <td>SD <td>Mean <td>SD </td></td></td>	SD <td>Mean <td>SD </td></td>	Mean <td>SD </td>	SD
LPG	0	0	645	160
Gasoline	445	85	765	226
Diesel	1784	402	1413	360
Total	2229	392	2823	616

Note: <sup>a</sup>bd<sup>a</sup> represents below limit of detection (LOD).

the sampling period. Figure 4 compares the measured and theoretical values obtained in the two seasons. The measured molar compositions of formaldehyde were all higher in summer than in winter, whereas seasonal change had no impact on the theoretical values due to the consistency of traffic frequency in Hong Kong. As a result, larger discrepancies between the measured and theoretical values were seen in summer, further supporting that photochemical reactions significantly contributed to the

formaldehyde production in the roadside locations. The largest difference of 19.0% was observed in LMX, followed by 16.6% and 12.7% in PCX and MKX, respectively. More regional sources of precursors of photochemical reaction products were expected in LMX due to its location. In addition, it is reasonable that the smallest discrepancy was observed in MKX, which is the most dense area among the three sites. VE is the most dominant source even though other primary sources could contribute the

**Table 7.** Molar ratio of  $C_1/C_2$  and  $C_2/C_3$  in the source-dominated, roadside, and ambient samples in Hong Kong

Source-Dominated Samples					
Source	Concentration ratio		Reference		
	$C_1/C_2$	$C_2/C_3$			
<b>Vehicular emission</b>					
Taxis	$1.8 \pm 0.16$	$14.0 \pm 9.0$	This study		
LD passenger cars	$1.3 \pm 0.15$	$28.5 \pm 17.5$	This study		
Mini-buses	$2.6 \pm 0.31$	$16.2 \pm 17.7$	This study		
Single-deck big buses	$1.7 \pm 0.42$	$10.1 \pm 8.3$	This study		
Double-deck big buses	$2.5 \pm 0.83$	$7.1 \pm 6.8$	This study		
Light- and heavy-duty vehicles	$3.0 \pm 0.15$	$21.3 \pm 10.1$	This study		
Roadway tunnel	$3.6 \pm 0.62$	$10.7 \pm 7.0$	(Ho et al., 2007)		
<b>Cooking emission</b>					
Chinese restaurant	1.0–1.2	12.2–14.5	(Ho et al., 2006)		
Hong Kong style fast food shop	4.1	— <sup>a</sup>	(Ho et al., 2006)		
Western fast food chain shop	0.51–0.82	7.9–10.2	(Ho et al., 2006)		
Western restaurant	1.5	7.1	(Ho et al., 2006)		
Korean BBQ restaurant	1.0	14.3	(Ho et al., 2006)		
<b>Incense burning emission</b>					
Temple yard	2.9–4.2	— <sup>b</sup>	(Ho and Yu, 2002)		
<b>Roadside Samples</b>					
Site	Sampling Period	Sampling Time	Concentration Ratio		Reference
			$C_1/C_2$	$C_2/C_3$	
Lok Ma Chau	Summer/winter 2003	3-Rush-hr average	$4.2 \pm 1.7$	$7.2 \pm 2.5$	This study
Mong Kok	Summer/winter 2003	3-Rush-hr average	$3.5 \pm 1.0$	$7.8 \pm 2.0$	This study
HKPU	Summer/winter 2003	3-Rush-hr average	$4.0 \pm 2.4$	$10.5 \pm 6.5$	This study
Central	1997–2000	Daily	$2.3 \pm 1.0$	— <sup>b</sup>	(Sin et al., 2001)
HKPU	1999–2000	Daily	2.2	— <sup>b</sup>	(Lee et al., 2001)
Clear Water Bay	Summer 2001	4-hr average	1.7–7.0	— <sup>b</sup>	(Ho and Yu, 2002)
<b>Ambient Samples</b>					
Site	Sampling Period	Sampling Time	Concentration Ratio		Reference
			$C_1/C_2$	$C_2/C_3$	
Tsuen Wan	Summer/winter 2003	3-hr average	$1.8 \pm 0.34$	$10.7 \pm 7.0$	This study
Tsuen Wan	1997–2000	Daily	$2.2 \pm 1.0$	—	(Sin et al., 2001)

Notes: <sup>a</sup>The concentrations of propionaldehyde were below LOD.

<sup>b</sup>No data for propionaldehyde are available.

carbonyls to this urban location. The discrepancies between the measured and theoretical values for formaldehyde were <10% in winter, reflecting a decrease of significance of photochemical reaction to the roadside locations. However, no particular trend on the compositions can be seen for the other carbonyls owing to the strong contributions of formaldehyde.

### Carbonyl concentration ratios

The concentration ratio of formaldehyde to acetaldehyde ( $C_1/C_2$ ) for both VE-dominated samples and roadside samples were tabulated in Table 7. The  $C_1/C_2$  ratio was used widely to distinguish the sources in urban and rural areas (Possanzini et al., 1996, Shepson et al., 1991, Feng et al., 2005). (Shepson et al., 1991) found that the  $C_1/C_2$  ratio was close to 0.7–3.0 in the atmosphere in the urban areas and up to 10 in the rural airs. For the roadside samples, the highest  $C_1/C_2$  ratio,  $4.2 \pm 1.7$  on average, was reported in LMX. MKX and PUX had the  $C_1/C_2$  ratios of  $3.5 \pm 1.0$  and  $4.0 \pm 2.4$  on average, respectively. Our values were slightly above the suggested range for the urban, explaining that rather than the VE, the biogenic input of formaldehyde from surrounding environments (e.g., from Mainland China) and the secondary photochemical formation can affect the roadside airs. The greatest influences were seen in the border area of LMX. The lowest  $C_1/C_2$  ratio determined in MKX also demonstrates that the regional transportation of pollutants was less significant to the downtown area. Even though the recommendation can fit to interpret the trends for our roadside samples, uncertainties could not be ignored when the range or absolute value of  $C_1/C_2$  ratios are used to distinguish local urban/rural airs. VE is one of the largest pollution sources in the urban areas. According to our findings in Hong Kong, the  $C_1/C_2$  ratios for the VE-dominated sources (1.3–3.0) were close to the maximum suggested value. For

the more VE-dominated samples collected in a roadway tunnel, the  $C_1/C_2$  ratio was  $3.6 \pm 0.62$  on average, which was even out of the suggested range (Ho et al., 2007). Other anthropogenic sources including cooking and incense burning also had a variety of  $C_1/C_2$  ratios (Ho and Yu, 2002, Ho et al., 2006).

Table 7 shows the concentration ratio of acetaldehyde to propionaldehyde ( $C_2/C_3$ ). The highest  $C_2/C_3$  ratio,  $10.5 \pm 6.5$  on average, was seen in PUX, whereas the lowest ratio,  $7.2 \pm 2.5$  on average, was found in LMX. (Feng et al., 2005) commented that propionaldehyde was expected to be associated only with anthropogenic emission sources, as a result a low molar ratio of  $C_2/C_3$  is typically found in the urban atmospheres. Our result disagreed with their conclusion because higher  $C_2/C_3$  ratios were found in the urban roadside locations. Few vascular plants also emit carbonyls including propionaldehyde into the atmosphere (Villanueva-Fierro et al., 2004). Besides, the  $C_2/C_3$  ratios for the VE-dominated samples greatly varied, ranging from 7.1 to 28.5. This suggests that the ratios may not be constant even for a particular emission source. The use of  $C_2/C_3$  molar ratio to distinguish biogenic and anthropogenic sources is thus questionable.

Figure 5 compares the concentration ratios of  $C_1/C_2$  and  $C_2/C_3$  measured in the two seasons. The  $C_1/C_2$  ratios were at least 1.5 times higher in summer than that in the winter. The variation in  $C_1/C_2$  ratios was also greater in the summer, which is consistent with the finding reported by (Sin et al., 2001). Both observations are consistent with higher contribution of biogenic emission and the secondary photochemical sources in hot weather. Higher  $C_2/C_3$  ratios were found in the three roadside locations in the winter. Again, the result was opposite to the suggestion by (Feng et al., 2005). The formations of propionaldehyde may not be limited to anthropogenic emission, and the contribution from the biogenic source of a regional scale should not be underestimated.

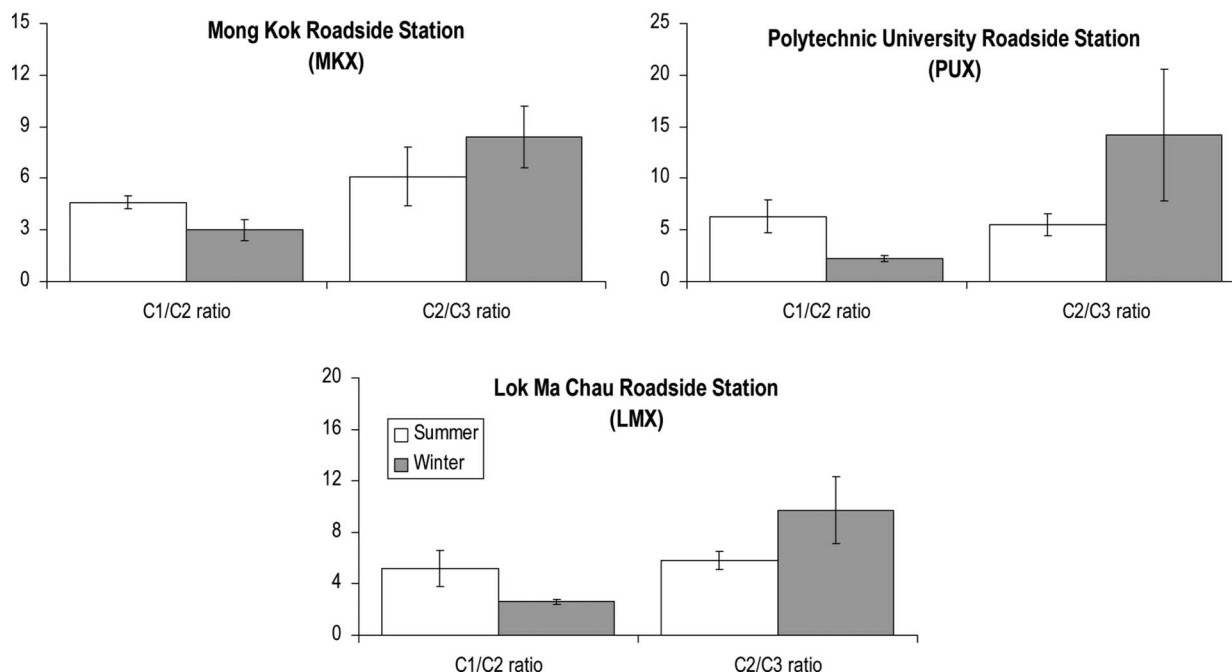


Figure 5. Seasonal variations of the  $C_1/C_2$  and  $C_2/C_3$  concentration ratios at the three roadside stations.

## Acknowledgments

This project is supported by the study Determination of Suspended Particulate & VOC Emission Profiles for Vehicular Sources in Hong Kong (Tender Ref. AS 02–342) funded by the Hong Kong Environment Protection Department (HKEPD), the Research Grants Council of Hong Kong (PolyU5204/07E), and the Hundred Talents Program (Observation and modeling of secondary organic aerosol formation in China [KZCX2-YW-BR-10]) of the Chinese Academy of Sciences.

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