

Diurnal and seasonal trends of carbonyl compounds in roadside, urban, and suburban environment of Hong Kong



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HIGHLIGHTS

- Total carbonyl concentrations decreased in order of roadside, urban, and suburban.
- Correlations of carbonyl compounds with NO, O₃, CO, etc. were investigated.
- Diurnal variations of carbonyls and other pollutants proved photochemical reaction.

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ABSTRACT

Seasonal and diurnal variations of carbonyl compounds were investigated in roadside (MK), urban (TW), and suburban (UST) environments in Hong Kong. Thirteen carbonyls (C1–C6) were identified and quantified in the samples. The average total quantified carbonyl concentrations decreased in the order of roadside ($12.16 \pm 3.52 \mu\text{g m}^{-3}$), urban ($10.45 \pm 4.82 \mu\text{g m}^{-3}$), and suburban ($5.14 \pm 3.35 \mu\text{g m}^{-3}$). Formaldehyde was the most abundant species, accounting for ~52%, ~52%, and ~46% of total measured carbonyls at MK, TW, and UST, respectively. At MK, the summer/winter ratios of most carbonyls were below one. The diurnal variations were associated with traffic flows, with high concentrations in daytime but low in nighttime. Good correlations were found between most carbonyls and carbon monoxide (CO), showing primary vehicular emission was the major source at the roadside location. In contrast, the summer/winter ratios of most carbonyls were larger than one at the urban site of TW and their carbonyls correlated well with secondary pollutant of ozone (O₃), indicating photochemical reactions contributed significantly in the formation of carbonyls, especially in summer. Distinct diurnal variations of carbonyls were observed at TW on a hazy winter day of 28 Jan 2012. Most carbonyl concentrations reached the first peak at noontime and had the second peak in the evening. The first peak was ascribed to be the products of photochemical reactions as maximum concentrations of nitrogen monoxide (NO) and O₃ occurred just before and after the carbonyl peak, respectively. The correlations among the carbonyl species were strong in summer but fair in winter at UST. Natural sources (e.g. biogenic) were usually the major source at the suburban, as far as its surrounding environment is concerned.

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1. Introduction

Carbonyls, consisting of a carbon atom double-bonded to an oxygen atom (C=O), are ubiquitous in tropospheric atmosphere.

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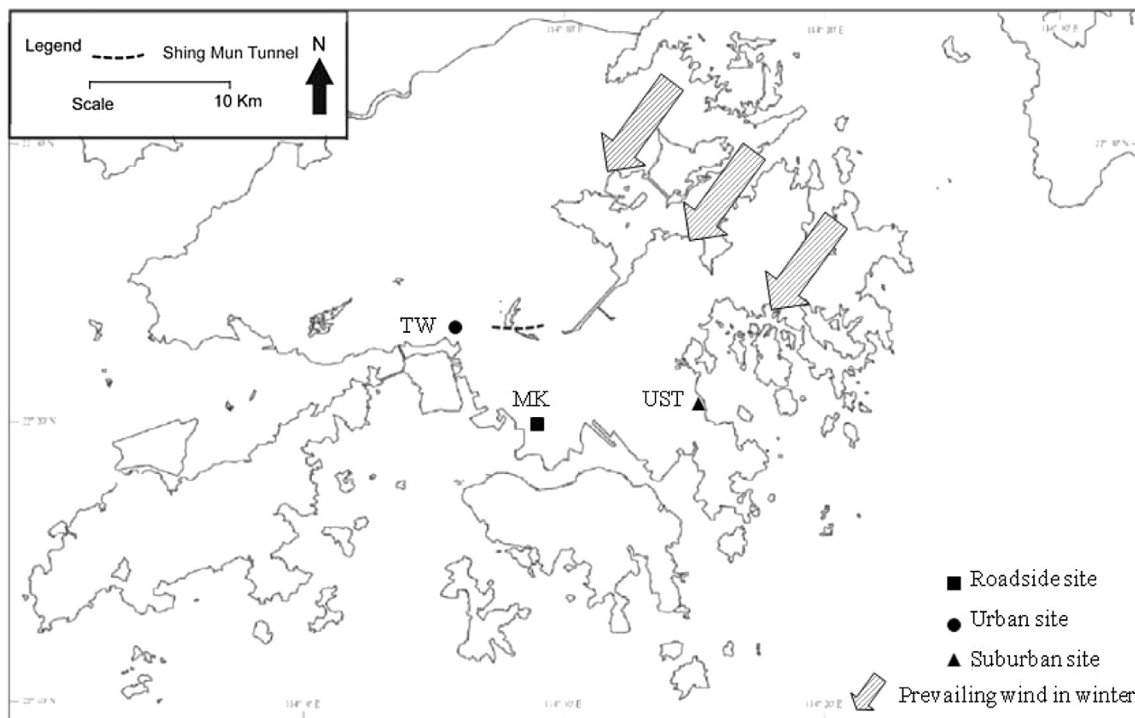


Fig. 1. A map showing the sampling sites in this study.

Carbonyls can be emitted from primary sources as residues from incomplete combustion or formed in atmosphere through secondary photo-oxidation processes of organic compounds (Lary and Shallcross, 2000). In addition, photolysis of carbonyls represented a significant source of free radicals (Carlier et al., 1986) and triggered the formation of ozone, peroxyacetyl nitrate and other oxidants (Carter, 1994), which are recognized as potential contributors to photochemical pollution. Thus, carbonyls play an important role in the secondary photochemical reactions in the troposphere and lower stratosphere, though their lifetimes are only in the order of a few hours to 1 day (Atkinson, 2000).

Many carbonyl compounds are classified to be toxic air pollutants (TAPs), such as formaldehyde and acetaldehyde. Formaldehyde is a probable human carcinogen (USEPA, 1999a) and acetaldehyde is also evidenced to be carcinogenic to animal (WHO, 2000). Acrolein causes eye irritations and odor annoyance, and exacerbates asthma (Borchers et al., 1999; WHO, 2000). Methyl ethyl ketone (MEK), one of the most abundant ketones in atmosphere, can be potentially oxidized to a neurotoxic metabolite (Key et al., 1977). The presence of carbonyls in the environment is thus of great concern with regard to their adverse effects on public health and environment.

A few studies on urban carbonyls were carried out in Hong Kong. The concentrations of C_1 – C_8 carbonyl compounds were measured at two urban sites from October 1997 to September 2000 by Sin et al. (2001). Formaldehyde was found to be the most abundant species (1.9 – $11.0 \mu\text{g m}^{-3}$), followed by acetaldehyde (0.3 – $7.7 \mu\text{g m}^{-3}$) and acetone (0.1 – $3.8 \mu\text{g m}^{-3}$). Photochemical reactions and vehicle emissions were believed to be the major source of formaldehyde and acetaldehyde (Ho et al., 2012; Sin et al., 2001). Formaldehyde and acetaldehyde were determined at roadside sites by Ho et al. (2002, 2012). The annual average concentration for formaldehyde and acetaldehyde were 4.53 and $2.05 \mu\text{g m}^{-3}$, respectively (Ho et al., 2002). Seasonal variation was observed from previous studies and it is found that formaldehyde concentration in summer was higher than that of winter. Photochemical reactions were believed to significantly contribute to the

formaldehyde production in roadside environment during summertime (Ho et al., 2012). The investigation of the primary emission of carbonyls from fresh vehicle emissions was carried out by Ho et al. (2007). The five most abundant carbonyls emitted by vehicles were, in decreasing order, formaldehyde, acetaldehyde, acetone, crotonaldehyde and MEK, contributing over 85% of the total measured carbonyls. Formaldehyde emission contributed more than 50% of the total measured carbonyl emissions during different measurement periods. However, large variability in carbonyl emissions was observed in this study.

The sources of carbonyls are complex, compound-dependent, and also vary with seasons, time of a day and locations. Further studies are necessary since we know very little as yet about the behavior of carbonyls in atmosphere (Louie et al., 2013). The objectives of the present study were to: 1) explore the spatial characteristics of speciated carbonyls in Hong Kong ambient air, 2) investigate the diurnal and seasonal variations of speciated carbonyls, and 3) identify the potential sources for carbonyls based on correlations with other pollutants and meteorological parameters.

2. Sampling method and chemical analysis

2.1. Sampling site and protocol

Three sites, Mong Kok (MK), Tsuen Wan (TW), and the campus of Hong Kong University of Science and Technology (UST), were selected to represent typical roadside, urban, and suburban environments of Hong Kong, respectively (Fig. 1). The MK and TW are the two stations within the air monitoring network of Hong Kong Environmental Protection Department (EPD). The MK station is at a transit position, where it is in the middle of several heavily-trafficked roads in an urban district. The carbonyl sampler was installed in a large shelter which was equipped with air conditioner, with the sampling inlet (3 m above the ground level) outside the shelter. The TW station is located in a district mixed with residential, commercial and light industrial activities. The carbonyl

sampler was installed on the rooftop of a four-floor building, approximately 12 m above the ground level. The sampling site of UST is located in a sparsely populated area. The nearest commercial building is 5 km away. The site is surrounded by mountains and marines, and thus it is deemed to measure “background” atmospheric properties.

Air samples were collected into silica cartridges impregnated with acidified 2,4-dinitrophenylhydrazine (DNPH) (Sep-Pak DNPH-silica, 55–105 mm particle size, 125 Å pore size, manufactured by Waters Corporation, Milford, MA). Twenty-four-hour (from 0:00 to 23:59) integrated samples were collected at the three sites simultaneously every third day in Aug 2011, Nov 2011, Feb 2012 and May 2012. A total of 41 samples were collected at each site. Three computer-controlled cartridge samplers (ATEC Model 8000-2 Cartridge Sampler, Malibu, CA) were employed in this study. The flow rate through each cartridge was regulated at 0.7 L min⁻¹, using an electronic mass flow controller. The results of breakthrough tests, carried out once per month, showed that no breakthrough was found at such sampling flow rates and sampling times. An ozone scrubber (Waters Corporation, Milford, MA) was installed in front of the DNPH-silica cartridge in order to prevent possible influence of ozone. A field blank was collected simultaneously for each sample to correct contaminations during sampling, transportation, and extraction. Collocated sample was collected at each site per month to calculate precision and evaluate biases. The precision of the collocated samples was within ~20% or better.

The diurnal variations of major carbonyls were investigated on two days (20 and 28 Jan 2012) at MK roadside site and four days (20, 28 Jan and 3, 21 Feb 2012) at TW ambient site. Seven air samples were consecutively collected every two hours during daytime (6:00–19:59) and one sample was collected for six hours during nighttime (18:00–05:59). The sampling and chemical analysis methods were same as the method of daily samples.

2.2. Analytical procedure

The sampled cartridge was eluted slowly with acetonitrile (ACN) into a 2 mL rinsed volumetric flask. One milliliter of the extract was then transferred into a clean auto-sampler amber vial for analysis. A reverse phase High Performance Liquid Chromatography (HPLC) system (Perkin Elmer Series 2000, Massachusetts 02451, USA) coupled with an ultra-violet (UV) detector operating at 360 nm was used for chemical analysis. The column was a Perkin Elmer ODS 5 μm pore size C-18 (4.6 mm × 250 mm). The mobile phase consisted of three solvent mixtures: (A) 6:3:1 (v/v/v) water/acetonitrile/tetrahydrofuran, (B) 4:6 (v/v) water/acetonitrile and (C) acetonitrile. The gradient program was 80% A/20% B for 1 min, followed by a linear gradient to 50% A/50% B in 8 min, 100% B for 10 min, 100% C for 6 min, and, finally, 100% C for 5 min. The flow rate was 2.0 mL min⁻¹ throughout the run. All solvents and water used were in HPLC grade (Duksan Pure Chemicals Co., Ltd, Gyeonggi-do, Korea) and Milli-Q grade, respectively. The calibration curve was established by five concentration points covering the levels of interest. One calibration standard was run for every ten samples to ensure the stabilization of the instrument. Carbonyls were identified and quantified by their retention times and peak areas of the corresponding calibration standards. The detection limits for target carbonyls were below 0.020 μg m⁻³.

The analytical procedures met the requirements of United States Environmental Protection Agency (USEPA) Method TO-11a (USEPA, 1999b). Sixteen carbonyl compounds were detected. However, acrolein and crotonaldehyde which showed further reaction with DNPH, were excluded (Ho et al., 2011). Additionally, acetone was found in breakthrough and thus excluded. Only

Table 1
The average seasonal carbonyl concentrations at the three sampling sites.

Sampling sites	C1	C2	nC3	MEK	iso + nC4	benz	iso-C5	nC5	o-tol	m-tol	p-tol	C6	2,5-DB	Total
	μg m ⁻³													
MK (Roadside)	Spring	5.81 ± 1.19	2.33 ± 0.74	0.41 ± 0.14	0.29 ± 0.34	0.33 ± 0.08	0.48 ± 0.63	0.29 ± 0.17	0.18 ± 0.03	0.04 ± 0.02	0.08 ± 0.04	0.11 ± 0.10	0.91 ± 0.85	11.12 ± 2.57
	Summer	6.87 ± 2.70	2.36 ± 1.41	0.43 ± 0.27	0.19 ± 0.18	0.34 ± 0.20	0.35 ± 0.25	0.55 ± 0.54	0.12 ± 0.03	0.06 ± 0.00	0.12 ± 0.09	0.32 ± 0.09	bd ^a	11.65 ± 5.38
	Autumn	7.41 ± 1.56	2.99 ± 0.68	0.37 ± 0.14	0.40 ± 0.30	0.23 ± 0.10	0.36 ± 0.16	0.74 ± 0.21	0.13 ± 0.04	0.08 ± 0.03	0.19 ± 0.08	0.37 ± 0.12	0.06 ± 0.03	13.33 ± 2.75
	Winter	5.76 ± 1.32	2.92 ± 0.67	0.60 ± 0.12	0.99 ± 0.46	0.40 ± 0.09	0.39 ± 0.13	0.60 ± 0.17	0.31 ± 0.06	bd ^a	bd ^a	bd ^a	0.64 ± 0.15	12.60 ± 2.33
TW (Urban)	All	6.47 ± 1.89	2.64 ± 0.96	0.45 ± 0.19	0.46 ± 0.45	0.32 ± 0.14	0.40 ± 0.34	0.55 ± 0.35	0.18 ± 0.09	0.06 ± 0.03	0.13 ± 0.09	0.37 ± 0.22	0.51 ± 0.74	12.16 ± 3.52
	Summer/Winter	1.19	0.81	0.72	0.19	0.85	0.90	0.92	0.38	NA ^b	NA ^b	0.50	NA ^b	0.92
	Spring	4.04 ± 1.22	1.79 ± 0.84	0.41 ± 0.17	0.22 ± 0.26	0.33 ± 0.13	0.30 ± 0.16	0.30 ± 0.28	0.20 ± 0.04	0.06 ± 0.08	0.05 ± 0.04	1.06 ± 0.04	0.59 ± 0.13	8.30 ± 2.78
	Summer	10.81 ± 2.60	1.53 ± 0.51	0.57 ± 0.29	0.34 ± 0.09	0.33 ± 0.08	0.52 ± 0.20	0.85 ± 0.18	0.52 ± 0.18	bd ^a	0.06 ± 0.02	1.06 ± 0.40	bd ^a	16.60 ± 3.74
UST (Background)	Autumn	3.97 ± 0.94	1.83 ± 0.53	0.34 ± 0.13	0.34 ± 0.38	0.19 ± 0.09	0.27 ± 0.16	0.43 ± 0.33	0.10 ± 0.03	bd ^a	0.10 ± 0.10	0.21 ± 0.07	bd ^a	7.79 ± 2.27
	Winter	3.62 ± 1.58	2.06 ± 0.87	0.41 ± 0.18	0.68 ± 0.42	0.28 ± 0.15	0.27 ± 0.13	0.42 ± 0.24	0.18 ± 0.12	0.40	0.27 ± 0.18	0.41 ± 0.24	bd ^a	8.51 ± 3.39
	All	5.74 ± 3.53	1.80 ± 0.70	0.44 ± 0.21	0.39 ± 0.34	0.28 ± 0.12	0.35 ± 0.19	0.52 ± 0.33	0.26 ± 0.20	0.06 ± 0.08	0.08 ± 0.08	0.47 ± 0.46	0.59 ± 0.13	10.45 ± 4.82
	Summer/Winter	2.99	0.74	1.38	0.50	1.17	1.91	1.80	2.88	NA ^b	0.16	2.59	NA ^b	1.95
UST (Background)	Spring	1.98 ± 0.78	0.88 ± 0.52	0.28 ± 0.42	0.20 ± 0.30	0.25 ± 0.29	0.29 ± 0.39	0.33 ± 0.58	0.12 ± 0.21	0.03 ± 0.00	0.05 ± 0.02	0.32 ± 0.69	bd ^a	5.13 ± 4.63
	Summer	2.64 ± 2.45	0.90 ± 1.02	0.21 ± 0.17	0.22 ± 0.32	0.24 ± 0.28	0.16 ± 0.18	0.23 ± 0.24	0.06 ± 0.03	bd ^a	bd ^a	0.15 ± 0.08	bd ^a	4.70 ± 4.60
	Autumn	2.63 ± 0.88	1.27 ± 0.41	0.18 ± 0.08	0.32 ± 0.24	0.11 ± 0.10	0.19 ± 0.11	0.29 ± 0.22	0.04 ± 0.02	bd ^a	0.05 ± 0.03	0.06 ± 0.02	bd ^a	5.12 ± 1.70
	Winter	2.35 ± 0.62	1.40 ± 0.33	0.35 ± 0.06	0.64 ± 0.26	0.23 ± 0.06	0.27 ± 0.09	0.34 ± 0.11	bd ^a	bd ^a	bd ^a	0.20 ± 0.02	bd ^a	5.64 ± 1.22
UST (Background)	All	2.40 ± 1.40	1.11 ± 0.66	0.25 ± 0.23	0.34 ± 0.32	0.21 ± 0.21	0.23 ± 0.22	0.29 ± 0.32	0.07 ± 0.12	0.03 ± 0.00	0.05 ± 0.02	0.20 ± 0.02	0.18 ± 0.42	5.14 ± 3.35
	Summer/Winter	1.12	0.64	0.59	0.34	1.01	0.57	0.67	NA ^b	NA ^b	NA ^b	NA ^b	NA ^b	0.83

^a Below detection limit.

^b Not applicable.

13 compounds were studied. They were formaldehyde (C1), acetaldehyde (C2), propionaldehyde (n-C3), methyl ethyl ketone (MEK), n-butyraldehyde/isobutyraldehyde (iso + nC4), benzaldehyde (benz), isovaleraldehyde (iso-C5), n-valeraldehyde (n-C5), o-tolualdehyde (o-tol), m-tolualdehyde (m-tol), p-tolualdehyde (p-tol), n-hexaldehyde (C6) and 2,5-dimethylbenzaldehyde (2,5-C6).

3. Results and discussion

3.1. Spatial variations of measured carbonyls in roadside, urban, and background environments

The average concentrations of carbonyl compounds measured at each site of Hong Kong were summarized in Table 1. The sum of measured carbonyl compounds at roadside MK ($12.2 \pm 3.5 \mu\text{g m}^{-3}$) and urban TW ($10.5 \pm 4.8 \mu\text{g m}^{-3}$) were close, while the value at rural UST ($5.1 \pm 3.4 \mu\text{g m}^{-3}$) was much lower. No statistical differences ($p > 0.05$) for all measured carbonyl compounds were found between MK and TW, except for acetaldehyde, however, all species at MK were statistically different ($p < 0.05$) with those at UST. This may imply that the origins of carbonyl compounds were different between urban and background environment. Both MK roadside air and TW urban air were contaminated by severely polluted plume, compared to UST rural air. Diesel-fueled buses, being characterized by high emission rates of formaldehyde and acetaldehyde, were believed to significantly contribute to the high carbonyl concentrations in urban atmosphere (Ho et al., 2007). In contrast, UST is located at an open area and faces a clean rural area on the east coast of Sai Kung with good dispersion. It is classified as rural coastal background with little residential and commercial developments nearby.

Formaldehyde was the most abundant carbonyl species, accounting for ~52%, ~52%, and ~46% of total measured carbonyl compounds in the roadside, urban, and background environments, respectively, followed by acetaldehyde (~21%, ~16%, and ~23%, respectively), as seen in Fig. 2. This is similar to the previous studies in Hong Kong (Ho et al., 2002), Guangzhou (Lü et al., 2009) and Shanghai (Huang et al., 2008). In this study, the average roadside formaldehyde concentration was $6.47 \mu\text{g m}^{-3}$, ranging from 3.76 to $11.14 \mu\text{g m}^{-3}$; the average urban concentration was $5.74 \mu\text{g m}^{-3}$, ranging from 1.96 to $15.39 \mu\text{g m}^{-3}$; while the average background concentration was $2.40 \mu\text{g m}^{-3}$, ranging from 0.73 to $7.47 \mu\text{g m}^{-3}$. For acetaldehyde, the average roadside concentration was $2.64 \mu\text{g m}^{-3}$, ranging from 1.14 to $5.09 \mu\text{g m}^{-3}$; the average urban concentration was $1.80 \mu\text{g m}^{-3}$, ranging from 0.75 to $4.39 \mu\text{g m}^{-3}$; while the average background concentration was $1.23 \mu\text{g m}^{-3}$, ranging from 0.15 to $6.80 \mu\text{g m}^{-3}$. The concentrations of remaining species were generally below $1.0 \mu\text{g m}^{-3}$ at all sites. The frequency of the occurrence of o/m-tolualdehyde at MK was the highest among three sites. A previous study (Ho et al., 2012) also found that the concentrations of o-tolualdehyde and m/p-tolualdehyde were the highest at MK among three roadside stations in Hong Kong (e.g., MK, LM, and PU), but they were much lower than those measured in diesel-vehicular-emission-dominated sites.

In roadside environment, nC3, MEK, iso-C5, and 2,5-DB comprised ~4% of the total quantified carbonyls for each, followed by iso + nC4 (~3%), benzaldehyde (~3%) and C6 (~3%). For the remaining species, each contributed less than 1% in the roadside atmosphere. In urban atmosphere, both iso-C5 and 2,5-DB occupied ~5% of the total carbonyls, followed by n-C3, MEK, and C6, comprising ~4% of total measured carbonyls each. The rest 10% were made up by remaining species. In background environment, the abundance of carbonyls tends to decrease substantially with an increase in carbon chain and the percentages were around 4–6% for

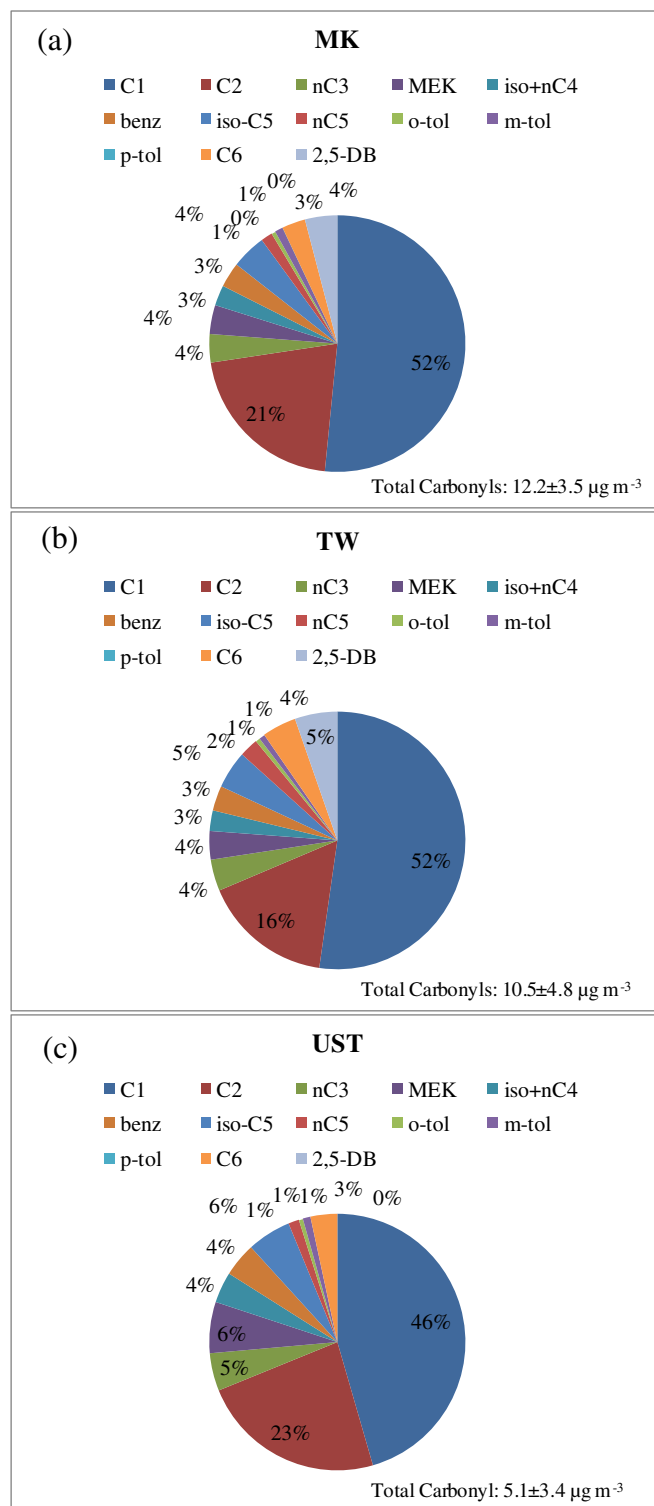


Fig. 2. Carbonyl compositions profiles at (a) MK, (b) TW, and (c) UST.

nC3, MEK, iso + nC4, benz, and iso-C5. nC5, o-tolualdehyde, m-tolualdehyde, p-tolualdehyde and 2,5-DB had proportions of 0–1% for each. C6 was below detection limit in about half of the samples and several species, e.g., o-tol, m-tol, p-tol, and 2,5-DB were below detection limits in more than ~75% of samples. Thus, they are not considered in the following discussion.

3.2. Seasonal variations

The average concentrations of individual carbonyl compounds in each season were summarized in Table 1. The meteorological parameters were recorded during sampling days, as shown in Table 2. According to the temperature, May, August, November, February were recognized to be spring, summer, autumn, and winter, respectively. The daily average temperature ranged from 28.7 °C to 30.9 °C during summer and from 12.3 °C to 19.9 °C in winter. The difference of temperature between summer and winter exceeded 10 °C. The average summer solar radiation per day (19.5 MJ m⁻²) was more than two times of that in winter (8.6 MJ m⁻²) and the bright sunshine hours (7.7 h) were higher than that of winter (4.5 h) as well.

The seasonal patterns of formaldehyde, acetaldehyde, MEK, and iso + nC4 were consistent among MK, TW, and UST sites, as shown in Table 1, implying these compounds were influenced by meteorological parameters like temperature, pressure, sunshine hours etc. Formaldehyde had its maximum value either in summer (UST) or autumn (MK) and the values were comparable. However, it was noticed that concentrations of formaldehyde were extremely high in summer at TW, exceeding the autumn value by a factor of ~3. This may suggest the occurrence of intensive photochemical reactions in summer urban ambient air. Acetaldehyde had higher concentrations in autumn and winter, compared to the values in spring and summer. For the rest of carbonyl compounds, such as propionaldehyde, benzaldehyde, isovaleraldehyde, valeraldehyde, o-tolualdehyde, m-tolualdehyde, p-tolualdehyde, hexaldehyde, 2,5-dimethylbenzaldehyde, the seasonal variations were not consistent among MK, TW, and UST, suggesting that their sources may associate with the involved micro-environments. For instance, the highest concentration of hexaldehyde was seen at UST in spring, which is even higher than the levels at MK and TW during the same season. Hexaldehyde had been identified as a marker of municipal sewage emission (Zhou et al., 2011) or tree leaves in China (Huang et al., 2010). However, more investigation is needed to conclude the sources of spring hexaldehyde at UST. As seen in Table 1, most summer/winter ratios were less than 1 at MK and UST, except those for formaldehyde (at both MK and UST) and butyraldehyde/isobutyraldehyde (at UST). In contrast, most summer/winter ratios were higher than 1 at TW, except for acetaldehyde. This also proves the presence of intense photochemical reactions in summer at TW.

It appears that the seasonal variations were inconsistent for carbonyl species in this study. Guo et al. (2004) also found that no common seasonal trends for ambient carbonyls in Hong Kong. Seasonal variations were reported from some of the previous ambient carbonyl measurements, however, the trend was found to vary from one place to another. For instance, formaldehyde reached its maximum level in southern California in autumn (Grosjean, 1991), while the levels peaked in summer in Rome (Possanzini et al., 1996), Eastern Finland (Viskari et al., 2000), and Mexico (Ceron et al., 2007). The main reason is due to specific meteorological parameters (e.g., temperature, relative humidity, solar

radiation and sunshine hours) in different cities. A previous study (Borbon et al., 2002) also claimed that local characteristics including the site typology and meteorological conditions have similar impacts on the lost processes or emission processes of carbonyls. Thus, meteorological parameters are necessary when carbonyls were investigated.

3.3. Source interpretation through correlations

Pearson correlations were used to investigate the inter-correlations among carbonyl species in summer and winter, separately, as shown in Tables 3–5. In summer, good correlations ($R > 0.8$) between most carbonyl species were found at MK, except for valeraldehyde and m-tolualdehyde, and hexaldehyde (Table 3). The pattern suggests that most of the carbonyls came from the same source in summer. The average concentrations of carbon monoxide (CO) and ozone (O₃) were 930 and 7 μg m⁻³, respectively, during the sampling period in summer. Formaldehyde, acetaldehyde, and MEK correlated well with O₃ and CO. CO was known as a primary emission, arising from incomplete combustion of nearby vehicle engines; while O₃ was mainly formed from photochemical reaction in tropical atmosphere. Thus the summertime carbonyls had two origins, which were primary emissions from vehicles and secondary pollutants from photochemical reaction. In addition, the ratio of C1/C2 was 3.2 ± 0.5, which was a little higher than the winter value of 2.0 ± 0.2, indicating significant formation of secondary carbonyls in summer. However, except isovaleraldehyde, most carbonyl compounds had poor correlations with the sunlight hour and solar radiation. This could be due to the vehicle emissions were dominant at the roadside environment. High loading of carbonyl pollution in air was found to be associated with the increase of reduced visibility hours per day in summer. In winter, most carbonyls, such as formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde/isobutyraldehyde, and valeraldehyde, were associated with nitrogen monoxide (NO), a primary emission from vehicles (especially diesel-fueled vehicles), instead of secondary products (e.g., O₃). This suggested that primary emissions from vehicles were major sources of carbonyls in winter.

Except for isovaleraldehyde, carbonyl compounds at TW (Table 4) had similar characteristics of inter-correlations with those at MK during summertime. However, most carbonyls correlated with secondary pollutant (O₃), instead of primary emissions like NO and CO. Based on above evidence, photochemical reaction was believed to play a more important role at urban ambient site than at a traffic-dominated site. The C1/C2 ratios were the highest at TW, with average value of 7.3 ± 1.5, which was a recommended value for existence of biogenic source of formaldehyde (Shepson et al., 1991; Possanzini et al., 1996). However, drawing a conclusion only based on the C1/C2 ratio is arbitrary because sources of carbonyls are complex. The C2/C3 ratios were further investigated and it showed a low average value of 2.9 ± 0.8 in summer, which was the lowest among three sites (Table 1) in this study. Propionaldehyde was believed to be associated only with anthropogenic emission. The low C2/C3 value in this study indicated

Table 2
Meteorological parameters in the sampling periods.

	Pressure (hPa)	Temperature (°C)	RH (%)	Cloud (%)	Rainfall (mm)	Reduced visibility (h)	Sunshine hours (h)	Solar radiation (MJ m ⁻²)	Wind direction	Wind speed (km h ⁻¹)
Spring	1009.4	26.1	79.8	70.4	11.6	4.8	5.4	16.7	98.0	17.6
Summer	1005.7	29.6	76.3	56.0	7.3	3.3	7.7	19.5	185.5	12.6
Autumn	1015.7	22.6	76.7	76.6	31.2	1.5	4.7	10.0	51.0	29.2
Winter	1017.5	15.6	82.8	80.7	0.9	5.6	4.5	8.6	41.0	24.8
All	1011.9	23.6	78.8	70.6	9.2	3.8	5.9	13.8	96.1	20.9

Table 3
Correlation coefficients at MK in summer and winter.

MK (summer)	C1	C2	nC3	MEK	iso + nC4	benz	i-C5	n-C5	o-tol	C6	O ₃	NO	CO
Formaldehyde	1.00												
Acetaldehyde	0.98	1.00											
Propionaldehyde	0.96	0.99	1.00										
Methyl ethyl ketone	0.96	0.91	0.87	1.00									
Butyraldehyde/isobutyraldehyde	0.79	0.82	0.84	0.67	1.00								
Benzaldehyde	0.94	0.94	0.94	0.85	0.88	1.00							
Isovaleraldehyde	0.69	0.81	0.86	0.51	0.75	0.75	1.00						
Valeraldehyde	-0.28	-0.26	-0.24	-0.39	-0.17	-0.15	-0.12	1.00					
m-Tolualdehyde	0.31	0.47	0.55	0.10	0.51	0.45	0.84	0.32	1.00				
Hexaldehyde	-0.11	-0.07	-0.05	-0.25	-0.18	-0.09	0.07	0.75	0.34	1.00			
O ₃	0.77	0.66	0.57	0.86	0.53	0.61	0.14	-0.55	-0.24	-0.61	1.00		
NO	-0.30	-0.33	-0.28	-0.39	0.04	-0.02	-0.19	0.64	0.02	0.31	-0.46	1.00	
CO	0.73	0.71	0.68	0.73	0.63	0.61	0.36	0.00	0.18	0.07	0.62	-0.27	1.00
MK (winter)	C1	C2	nC3	MEK	iso + nC4	benz	i-C5	n-C5	C6	O ₃	NO	CO	
Formaldehyde	1.00												
Acetaldehyde	0.92	1.00											
Propionaldehyde	0.85	0.95	1.00										
Methyl ethyl ketone	-0.46	-0.21	-0.01	1.00									
Butyraldehyde/isobutyraldehyde	0.80	0.83	0.79	-0.12	1.00								
Benzaldehyde	0.18	0.44	0.60	0.65	0.44	1.00							
Isovaleraldehyde	0.16	0.45	0.57	0.65	0.48	0.97	1.00						
Valeraldehyde	0.93	0.90	0.80	-0.39	0.77	0.19	0.16	1.00					
Hexaldehyde	0.64	0.68	0.62	-0.28	0.72	0.27	0.27	0.75	1.00				
O ₃	-0.32	-0.40	-0.47	0.06	-0.57	-0.50	-0.51	-0.23	-0.43	1.00			
NO	0.85	0.81	0.76	-0.36	0.77	0.30	0.27	0.79	0.42	-0.54	1.00		
CO	0.39	0.65	0.60	0.04	0.60	0.41	0.55	0.40	0.51	-0.58	0.40	1.00	

Bold signifies ratios with correlation coefficients higher than 0.7.

anthropogenic emission, most likely from the nearby light industries. The result thus concludes that the source of carbonyl is complex in summer and it is most likely a mixture of vehicle emission, evaporation of industrial activities and solvents, and photochemical reaction. Similar to MK, formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde/isobutyraldehyde, and valeraldehyde correlated with each other and all of them were associated with NO in winter. It indicated that primary vehicular emissions were major sources. Since formaldehyde also correlated

with temperature and nitrogen dioxide (NO₂), it was concluded that at least parts of formaldehyde associated with photochemical reaction in the atmosphere. The average C1/C2 ratio was 1.8 ± 0.2 , which is a typical value for urban pollutants as previous study reported (Sin et al., 2001; Feng et al., 2004; Liu et al., 2006; Pang and Mu, 2006; Santarsiero and Fuselli, 2008; Lü et al., 2009, 2010), suggesting the sampling sites are consistent to other urban environments in the world. The average C2/C3 ratio was 5.0 ± 0.8 , a comparable value with most occasions at TW and MK.

Table 4
Correlation coefficients at TW in summer and winter.

TW (summer)	C1	C2	nC3	MEK	iso + nC4	benz	i-C5	n-C5	m-tol	C6	O ₃	NO	CO
Formaldehyde	1.00												
Acetaldehyde	0.71	1.00											
Propionaldehyde	0.93	0.84	1.00										
Methyl ethyl ketone	0.74	0.71	0.69	1.00									
Butyraldehyde/isobutyraldehyde	0.74	0.43	0.65	0.40	1.00								
Benzaldehyde	0.90	0.78	0.96	0.55	0.73	1.00							
Isovaleraldehyde	0.03	0.02	-0.10	0.07	-0.15	-0.12	1.00						
Valeraldehyde	0.68	0.48	0.56	0.65	0.35	0.48	0.33	1.00					
m-Tolualdehyde	-0.56	0.01	-0.45	-0.22	-0.68	-0.51	-0.07	-0.34	1.00				
Hexaldehyde	0.13	-0.22	-0.18	0.08	0.11	-0.15	0.61	0.28	-0.15	1.00			
O ₃	0.85	0.88	0.94	0.74	0.49	0.88	0.06	0.72	-0.33	-0.17	1.00		
NO	-0.08	-0.17	0.06	-0.20	-0.04	0.07	-0.60	-0.32	-0.12	-0.20	-0.06	1.00	
CO	0.69	0.67	0.82	0.68	0.23	0.71	-0.29	0.34	-0.19	-0.33	0.77	0.33	1.00
TW (winter)	C1	C2	nC3	MEK	iso + nC4	benz	i-C5	n-C5	C6	O ₃	NO	CO	
Formaldehyde	1.00												
Acetaldehyde	0.97	1.00											
Propionaldehyde	0.92	0.95	1.00										
Methyl ethyl ketone	-0.32	-0.22	-0.26	1.00									
Butyraldehyde/isobutyraldehyde	0.85	0.86	0.96	-0.34	1.00								
Benzaldehyde	0.53	0.59	0.62	0.49	0.61	1.00							
Isovaleraldehyde	0.37	0.44	0.41	0.67	0.37	0.95	1.00						
Valeraldehyde	0.76	0.78	0.91	-0.34	0.97	0.58	0.29	1.00					
Hexaldehyde	0.62	0.64	0.79	-0.42	0.92	0.44	0.17	0.95	1.00				
O ₃	-0.39	-0.34	-0.31	-0.22	-0.30	-0.63	-0.70	-0.13	-0.18	1.00			
NO	0.96	0.93	0.94	-0.39	0.92	0.54	0.35	0.81	0.77	-0.47	1.00		
CO	0.84	0.84	0.75	-0.11	0.58	0.47	0.42	0.42	0.31	-0.53	0.80	1.00	

Bold signifies ratios with correlation coefficients higher than 0.7.

Table 5
Correlation coefficients at UST in summer and winter.

UST (summer)	C1	C2	nC3	MEK	iso + nC4	benz	i-C5
Formaldehyde	1.00						
Acetaldehyde	0.99	1.00					
Propionaldehyde	0.93	0.94	1.00				
Methyl ethyl ketone	0.87	0.84	0.72	1.00			
Butyraldehyde/isobutyraldehyde	0.73	0.80	0.80	0.43	1.00		
Benzaldehyde	0.87	0.88	0.91	0.54	0.82	1.00	
Isovaleraldehyde	0.91	0.95	0.85	0.72	0.89	0.85	1.00
UST (winter)	C1	C2	nC3	MEK	iso + nC4	benz	i-C5
Formaldehyde	1.00						
Acetaldehyde	0.80	1.00					
Propionaldehyde	0.53	0.89	1.00				
Methyl ethyl ketone	0.56	0.67	0.41	1.00			
Butyraldehyde/isobutyraldehyde	0.66	0.79	0.81	0.41	1.00		
Benzaldehyde	0.29	0.60	0.51	0.81	0.42	1.00	
Isovaleraldehyde	0.12	0.42	0.33	0.71	0.04	0.84	1.00

Bold signifies ratios with correlation coefficients higher than 0.7.

The correlation among all species was very good in summer and fair in winter at UST (Table 5). All carbonyl compounds, except MEK, correlated with each other in summer, with correlation coefficients larger than 0.70. Carbonyls were found to associate with RH, with increase of concentrations and decrease of RH (from 83% to 64%). Good correlations were found among MEK, benzaldehyde, and isovaleraldehyde and also among acetaldehyde, propionaldehyde, and butyraldehyde/isobutyraldehyde in winter. Formaldehyde only associated with acetaldehyde. The average C1/C2 ratio (1.7 ± 0.3) was much lower in winter than that (3.7 ± 1.0) in summer. The C2/

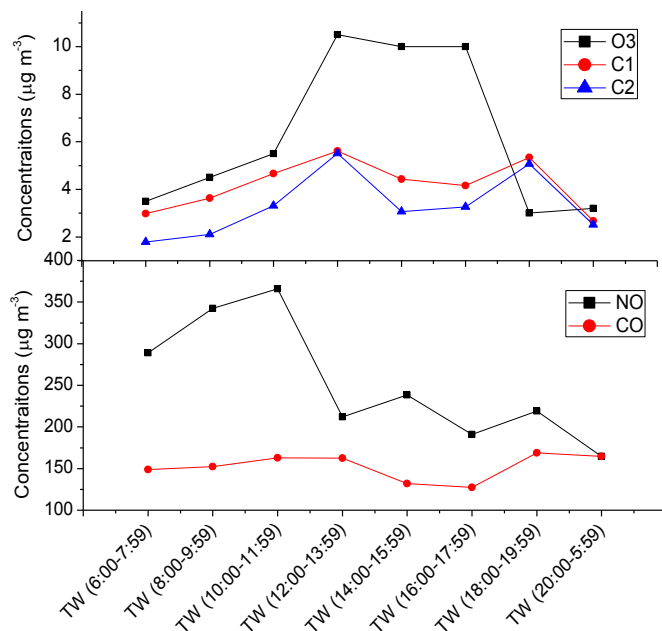


Fig. 4. Diurnal variations of various pollutants at TW on a hazy day (28 Jan 2012).

C3 value was very close in summer (3.8 ± 1.5) and winter (4.0 ± 0.4). Natural sources (e.g. biogenic sources) were usually the major source at UST, as far as its surrounding environment is concerned.

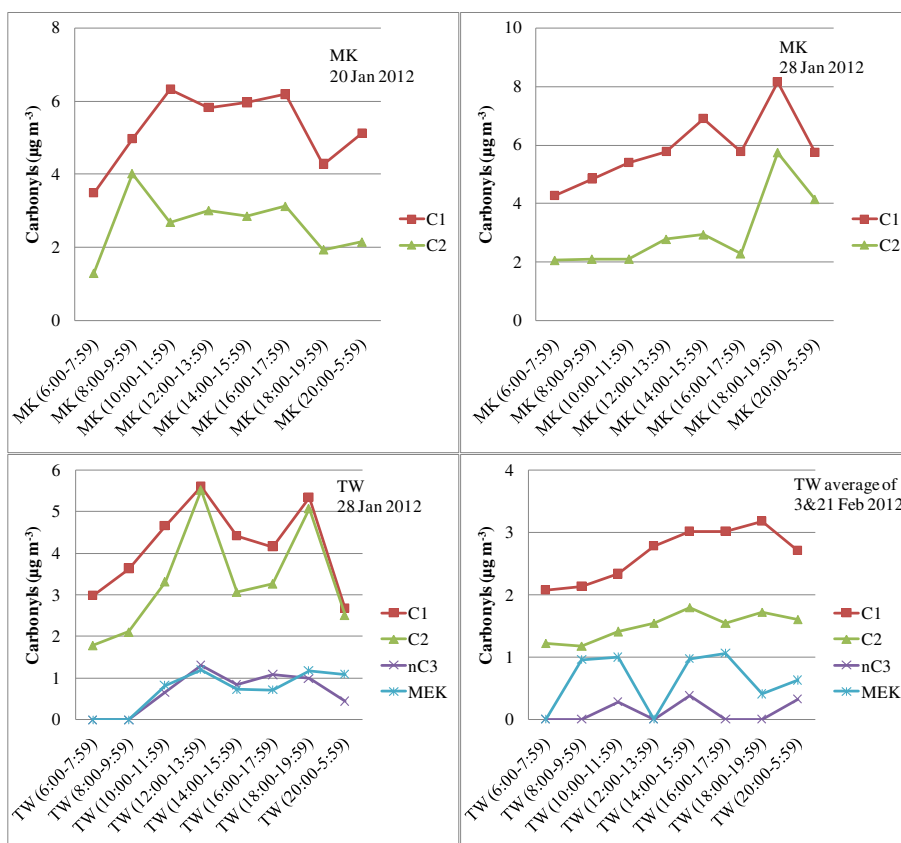


Fig. 3. Diurnal variations of carbonyls at MK and TW.

Table 6
Meteorological parameters on 20, 28 Jan 2012 and 3, 21 Feb 2012.

	Pressure (hPa)	Temperature (°C)	RH (%)	Cloud (%)	Rainfall (mm)	Reduced visibility (h)	Sunshine hours (h)	Solar radiation (MJ m ⁻²)	Wind direction	Wind speed (km h ⁻¹)
20-Jan-12	1015.5	17.4	86	86	–	4	1.2	8.54	60	33.2
28-Jan-12	1016.1	16.7	86	44	–	6	8	16.84	40	16.8
3-Feb-12	1022.5	14.5	79	88	Trace	2	0.1	5.31	40	26.2
21-Feb-12	1014.1	17.3	84	88	1.7	0	0.2	7.25	50	23.5

3.4. Diurnal variations

The diurnal patterns of carbonyl compounds were evident at MK on 20 Jan (Fig. 3), with high concentrations during daytime and low during nighttime. This pattern is similar with the previously monitored traffic fluctuations at MK (Ho et al., 2012). The average traffic flow rate was 2646 ± 646 per hour in the morning (8:00–11:00) and 3089 ± 533 per hour in the afternoon (15:00–18:00). Diesel-fueled vehicles accounted for ~45% and ~47% of the total vehicle numbers, respectively. Thus the concentrations of carbonyl compounds remained high levels from 8:00 to 18:00 and relatively low during nighttime, as seen from Fig. 3.

Distinct diurnal variations in carbonyl concentrations were seen at TW on 28 Jan (Fig. 4). The carbonyl concentration showed a maximum concentration at noon and early afternoon (12:00–13:59), a gradual decrease in the afternoon and a second peak in the evening (18:00–19:59). The meteorological data was examined on 28 Jan. it was noticed the day was characterized by low visibility, low wind speed and low amount of cloud, compared to the other days in Table 6. High concentrations of PM_{2.5} and PM₁₀ were recorded at several EPD air monitoring stations as well. It was a winter hazy day. However, the total bright sunshine hours were long (eight hours) and the daily solar radiation (16.8 MJ m^{-2}) was high, both exceeding the values in the other days by a factor of two. The first carbonyl peak may arise from photochemical reactions of primary pollutants, which was confirmed by the diurnal variations of NO and O₃, as seen in Fig. 4. Early morning traffic increased the emissions of both nitrogen oxides and volatile organic compounds (VOCs), thus a maximum concentration of NO was observed in the morning. As the sunlight became more intense at noon, nitrogen dioxide was broken down and its by-products of ozone formed in the afternoon (12:00–18:00). At the same time, some of the NO₂ can react with VOCs to produce toxic chemicals such as carbonyls and peroxyacetyl nitrate (PAN). As the sun went down, the production of O₃ was halted. The O₃ that remained in the atmosphere was then consumed by several different reactions. The second carbonyl peak was due to the evening traffic rush hour, which can be proved by the presence of CO peak during the same period.

The diurnal patterns of carbonyl compounds were different at TW on the other dates (e.g., 3 & 21 Feb 2012 in Fig. 3), where a minor peak was observed in mid-afternoon (14:00–15:59) in the daytime. This reflects to an accumulation of pollutants generated by the traffic and less photochemical formation of secondary carbonyls during the short sunshine hours according to the record. The diurnal pattern of carbonyls at MK on 28 Jan, 2012 was influenced by the hazy day, expressing different characteristics from normal date (20 Jan, 2012).

4. Conclusions

The concentrations of thirteen carbonyls were determined at three sampling sites (i.e. MK, TW, and UST) in Hong Kong for an one-year monitoring in 2011/2012. The temporal and diurnal variations were determined for carbonyl compounds. Potential pollution sources were interpreted through correlations analysis,

calculations of carbonyls ratios (i.e., C1/C2, C2/C3, summer/winter), and statistical methods. Most carbonyls at MK were correlated with each other and associated with primary vehicular gas emissions, suggesting they were from identical sources. Combined sources for the carbonyls were suggested at TW, including emissions from fueled-vehicles, industries and photochemical reactions. The carbonyls pattern at suburban site of UST showed background environment characteristics.

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