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Seasonal variation of carbonyl compound concentrations in urban area of Hong Kong

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Abstract

Ambient levels of carbonyls were determined at the roadside urban station of the Hong Kong Polytechnic University (HKPU) campus and it was the first systematic investigation of carbonyls at a roadside station in Hong Kong. A 12-month monitoring program for carbonyl compounds was carried out during April 1999–April 2000. Ten carbonyl compounds were quantified in this study. The most abundant carbonyl compound was formaldehyde, followed by acetaldehyde and acetone. The 24-hour average concentrations of formaldehyde and acetaldehyde were 4.13 and 2.01 $\mu g/m^3$. Most carbonyls have higher average concentrations at Tsuen Wan (TW) Toxic Air Pollutants (TAPs) monitoring station during summertime due to the addition of industrial emission from the nearby industrial area. Characterization of the roadside concentrations of carbonyl compounds was compared with the long-term ambient air quality monitoring data acquired by Hong Kong Environmental Protection Department (HKEPD) under TAP Monitoring Programme. Seasonal variations and winter/summer ratios at the monitoring station are discussed. Correlations and statistical analysis of the carbonyls were performed and comparison of carbonyl compounds concentrations at roadside and TAP monitoring stations determined.

Keywords: Carbonyl compounds; Seasonal variation; Correlation; Hong Kong

1. Introduction

Due to the large population (6.5 million) and limited area, Hong Kong is one of the most densely populated cities in the world. The limitation of available land and the various industrial developments, cause the high levels of air pollutants which may in turn affect the health of the citizens. Air quality has become an issue of major concern in Hong Kong. Carbonyl compounds are common constituents in urban atmospheres and are known to be toxic and carcinogenic (WHO, 1987). Significant levels of carbonyls in the Hong Kong atmosphere are directly emitted by motor vehicles. Hong Kong has very heavy vehicle traffic. Carbonyls are among the major species of organic compounds involved in photochemical air pollution since aldehydes and ketones play an important role as products of photooxidation of gas-phase hydrocarbons under a stronger solar radiation and higher temperature (Baez et al., 1995; Grosjean et al., 1990; Hoekman, 1992). Despite their role in urban air quality and health hazard assessment, reducing carbonyls have received little attention in air pollution monitoring programs to date (Possanzini et al., 1996). Formaldehyde is the most abundant atmospheric aldehyde, followed by acetaldehyde (Williams et al., 1996; Muller, 1997). Carbonyl

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compounds are toxic, particularly aldehydes (Carlier et al., 1986), and the most observed toxic effects are irritation of the skin, eyes and nasopharyngeal membranes. More seriously, formaldehyde and acrolein are suspected carcinogens.

A one-year monitoring program starting from April 1999 to April 2000 was performed at a roadside urban station in Hong Kong Polytechnic University (HKPU). The objective of this study is to characterize carbonyl compounds at a roadside station, which is not routinely done in Hong Kong. Since 1997, Hong Kong Environmental Protection Department (HKEPD) initiated monitoring of toxic air pollutants (TAPs) at Central/Western (CW) and Tsuen Wan (TW) monitoring stations. The correlations of carbonyl compounds at the roadside station were determined. The concentrations measured at this roadside study were compared with two TAPs stations (CW and TW) operated by HKEPD. The obtained database is useful to fill up the gap in the air quality data and for the attributions of source emissions of TAPs in urban area.

2. Experimental

2.1. Study site

The 24-hour carbonyl samples were collected on podium level at the HKPU for 12 months. It is about 6 m above ground level, at the same level and about 8 m away from the main elevated traffic road. The station is adjacent to Hong Chong Road, which leads to the Cross Harbour Tunnel. The traffic volume of the road is extremely high with more than 170,000 vehicles per day. Two other EPD air quality monitoring stations chosen for data comparison were located at CW and TW separately. CW Monitoring Station is classified as an urban residential/commercial area while TW Monitoring Station is classified as a mixed urban residential, commercial and industrial area. The samples were collected on the rooftop of 18 m (4 floors) and 17 m (4 floors) tall buildings, respectively.

2.2. Sampling and analysis

The sampling period was one year, covering the period from April 1999 to April 2000 and two weeks intensive sampling was carried out in January 2000. The climate in Hong Kong is sub-tropical and the seasons of autumn and spring are usually short. Therefore, we defined winter season as including November, December, January and February; while summer season includes May, June, July and August. Strong monsoon wind and dry weather characterize winter seasons. In the summer, it is hot and humid with occasional showers and thunderstorms. The prevailing winds in Hong Kong are mainly northeasterly especially in wintertime.

Table 1
The operating conditions of HPLC

Solvent A:	Water/CH_3CN/tetrahydrofuran (75/15/10 v/v)
Solvent B:	CH_3CN/water (55/45 v/v)
Flow rate:	1.5 ml/min
Column:	A 3.9 × 150 mm C18 column (Nova-Pak, Waters, Inc.)
Detector:	Variable wavelength ultraviolet, set to 360 mm

Carbonyl compounds in air were sampled at 60–80 ml/min for 24 hours using a silica cartridge impregnated with acidified 2,4-dinitrophenylhydrazine (Waters Sep-Pak DNPH–silica), which was very reactive toward carbonyls. No breakthrough was found within this flow rate. The flow rate through the cartridges was measured with a rotameter before and after each sampling period. The rotameter was calibrated in the laboratory against a soap bubble flow meter. An ozone scrubber was connected before DNPH–silica cartridge in order to prevent the interference of ozone. All cartridges were stored in a refrigerator at 4°C after sampling. The carbonyl samples were shipped in a cooler with blue ice to Desert Research Institute (DRI), Reno, NV for analysis using high-performance liquid chromatography (HPLC) (USEPA Method TO-11, 1987). The operating conditions of HPLC are shown in Table 1. Typically C_1–C_8 carbonyl compounds, including benzaldehyde, are measured effectively by this technique with a detection limit of ~0.2 ppbv.

2.3. Quality assurance and control

Identification and quantification of carbonyl compounds were based on retention times and peak areas of the corresponding calibration standards, respectively. The instrument was calibrated using five standard concentrations covering the concentration of interest for ambient work. Cartridge collection efficiency was determined with two cartridges in series; over 98% of carbonyl compounds were found in the first cartridge. The relative percent deviations (RPDs) of replicates were within 13% and the RPD of co-located samples were below 25%. Replicate analysis was performed for 10% of the samples randomly selected from previously analyzed groups for precision checking. The precision of replicate analysis was within ±10% for concentrations of 1 μg/ml and within 20% for concentrations near 0.5 μg/ml. Spiked recovery of carbonyl–DNPH standards should be within 100 ± 10%.

3. Results and discussion

3.1. Characterization of carbonyl compounds

Motor vehicle exhaust is expected to be the most important source of carbonyl compounds, they are also the key compounds of photochemically generated air pollution (Carlier et al., 1986). In our study, 10 different carbonyl compounds were quantified at HKPU roadside station. A total of 41 samples were collected. Formaldehyde is the most abundant atmospheric aldehyde, followed by acetaldehyde, acetone and benzaldehyde. The annual average formaldehyde concentration was 4.13 $\mu g/m^3$, ranged from 0.99 to 11.34 $\mu g/m^3$, average acetaldehyde concentration was 2.01 $\mu g/m^3$, ranged from 0.12 to 6.75 $\mu g/m^3$. The third most abundant carbonyl was acetone with an average concentration of 1.43 $\mu g/m^3$ and the average concentration of benzaldehyde was 1.06 $\mu g/m^3$. The summary statistics of carbonyl compounds are shown in Table 2. Concentrations of minor carbonyls, such as propionaldehyde, valeraldehyde, *m*-tolualdehyde, hexaldehyde, methyl ethyl ketone (MEK) and butyraldehyde were usually below 0.9 $\mu g/m^3$ in the roadside atmosphere at the HKPU station.

3.2. Seasonal variation

The levels of carbonyl compounds are dependent on the meteorological conditions (temperature, wind speed and solar irradiation, etc.). During summer, the high level of photochemical activities resulted in increased levels of some carbonyl compounds. The seasonal variation of carbonyls is shown in Fig. 1, and summer to winter ratios (S/W) are shown in Table 3. Average concentrations of formaldehyde and acetaldehyde at HKPU station was significantly higher in summer. Atmospheric photooxidation was an important secondary source of these carbonyls. They were produced photochemically at a higher level in summer, while direct vehicular emissions were the principal source of these carbonyls in winter. Table 4 gives a summary of temperature and solar radiation during the sampling period. It was found that the levels of carbonyl compounds increased as the ambient temperature or solar radiation increased. Also, the well-ventilated summer condition let the pollutants easily transport to our monitoring stations when compared to stagnant winter condition. S/W of formaldehyde and acetaldehyde were 2.3 and 1.7, respectively. However, S/W ratios of some carbonyls were below 1 (S/W of acetone = 0.38 and S/W of valeraldehyde = 0.09). The low concentrations of these carbonyls in the summer were due to the photolysis of these carbonyls to form hydroxyl radicals (Anderson et al., 1996; Christensen et al., 2000) and faster vertical mixing of urban emissions for this species. Large mixing flux in summer facilitates an effective dispersion of pollutants, clean oceanic air brought by southwest prevailing wind in summer could favor the removal and dilution of ambient aldehydes.

Table 2
Statistical summary of carbonyl compounds at HKPU station

Compounds	Mean ± S.D. ($\mu g/m^3$)	Maximum ($\mu g/m^3$)	Minimum ($\mu g/m^3$)
Formaldehyde	4.13 ± 2.32	11.34	0.99
Acetaldehyde	2.01 ± 1.20	6.75	0.12
Acetone	1.43 ± 1.58	6.55	0.01
Propionaldehyde	0.24 ± 0.18	0.87	0.01
Benzaldehyde	1.06 ± 0.51	2.32	0.28
Valeraldehyde	0.24 ± 0.38	2.23	0.01
m-Tolualdehyde	0.11 ± 0.15	0.85	0.02
Hexaldehyde	0.89 ± 0.72	4.06	0.02
MEK	0.42 ± 0.45	1.70	0.01
Butyraldehyde	0.15 ± 0.10	0.56	0.01

3.3. The concentration ratios of carbonyl compounds

Formaldehyde/acetaldehyde and acetaldehyde/propionaldehyde concentration ratios were measured. The ratios show large variations and the average value for formaldehyde/acetaldehyde was 2.05 which was quite similar to the study reported by Baez et al. (1995) (ratio = 2.33). It should be pointed out that formaldehyde/acetaldehyde ratios usually vary from 1 to 2 for urban areas to about 10 for rural (Shepson et al., 1991; Possanzini et al., 1996). However, some studies (Grosjean, 1992) reported that the ratios often show large variations and caution should be exercised when using such ratios. Acetaldehyde/propionaldehyde ratios should be used as indicators of anthropogenic origin for ambient carbonyls, since propionaldehyde was believed to be associated only with anthropogenic emissions. Acetaldehyde/propionaldehyde would be high in rural atmospheres and low in polluted urban air. The ratio of acetaldehyde/propionaldehyde was 8.38 at HKPU station. Its value was larger than some urban cites (Rome = 5.2; Possanzini et al., 1996). It implied that in the HKPU station, anthropogenic emission was the major source of carbonyls.

3.4. Correlations of carbonyl compounds

The correlations among 10 carbonyl compounds at HKPU roadside station during one-year monitoring program and during winter intensive monitoring are shown in Tables 5 and 6. Strong correlation between formaldehyde and acetaldehyde ($R = 0.80$), especially in the intensive winter sampling periods ($R = 0.86$) between December 1999 and January 2000, implies that these organic compounds came from the same sources

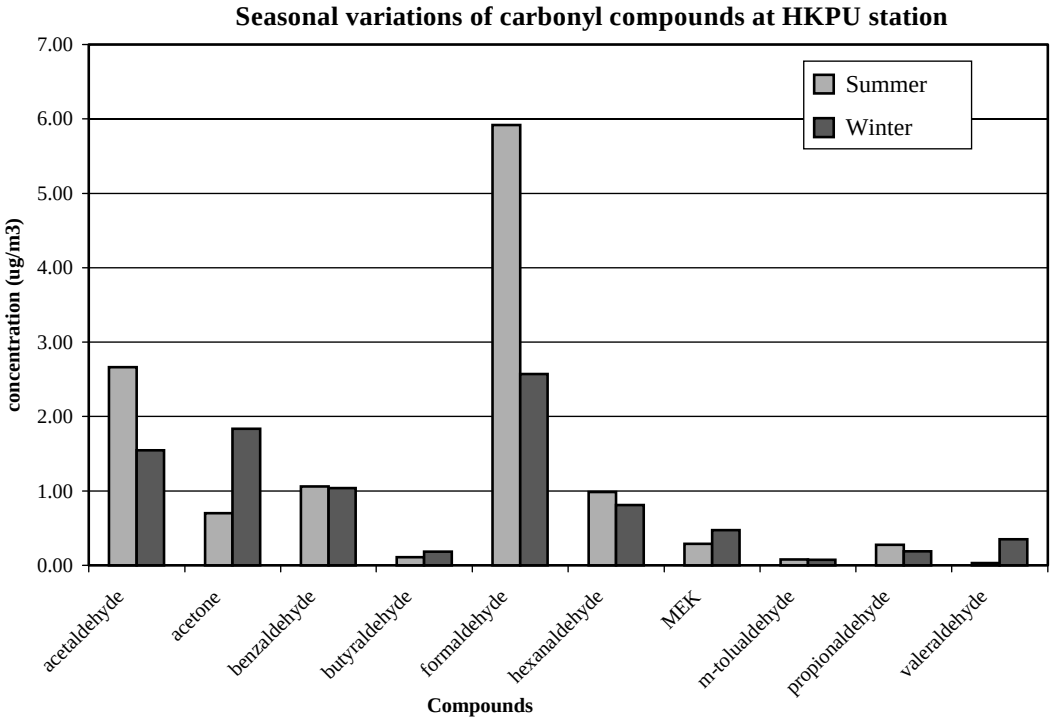

Fig. 1. The seasonal variation of carbonyl compounds at HKPU station.

Table 3
S/W of carbonyl compounds at HKPU station

Compounds	Summer	Winter	Mean S/W
Formaldehyde	5.92±1.64	2.57±1.55	2.30
Acetaldehyde	2.67±0.77	1.55±0.61	1.72
Acetone	0.70±0.78	1.84±1.63	0.38
Propionaldehyde	0.28±0.11	0.19±0.17	1.50
Benzaldehyde	1.06±0.65	1.04±0.33	1.02
Valeraldehyde	0.03±0.03	0.35±0.48	0.09
m-Tolualdehyde	0.08±0.07	0.08±0.05	1.03
Hexaldehyde	0.99±0.72	0.81±0.84	1.22
MEK	0.29±0.50	0.47±0.44	0.61
Butyraldehyde	0.11±0.06	0.18±0.10	0.60

Table 4
Summary of selected carbonyls concentrations and general weather conditions at PolyU station for samples acquired between April 1999 and April 2000 ($n = 41$) (concentrations in $\mu g/m^3$)

	Formaldehyde	Acetaldehyde
Summer (May–August)	5.64±1.42	2.46±0.43
Winter (November–February)	2.82±1.35	1.44±0.66
	Summer	Winter
Global solar radiation (MJ/m^2)	14.4±1.75	10.5±1.71
Monthly average temperature (°C)	27.8±1.99	17.9±2.99

(vehicles exhaust) during wintertime. Good correlations of carbonyls were found in the winter intensive sampling, except acetone. These agree with the study of Possanzini et al. (1996), vehicular exhaust was the primary source in winter while both vehicular exhaust and photochemical reactions were the major sources in summer. Lower correlations were found for one-year monitoring because of the photochemical degradation during high solar radiation in summertime and the vertical mixing of the pollutants were different in summer- and wintertime. The reaction rate (photochemical generation and photolysis) of each carbonyl were different, therefore, the variations of the concentrations of carbonyls in summertime were large. Acetone comes from both anthropogenic and biogenic emissions, recent study (Singh et al., 2000) reported that the global acetone mixing ratio was predominantly biogenic. Low correlations between acetone and other carbonyls at wintertime maybe due to the pollutant brought by the northeast prevailing wind in winter.

Table 5
Correlations of carbonyl compounds at HKPU roadside station for one-year monitoring

Compounds	1	2	3	4	5	6	7	8	9	10
Formaldehyde (1)	1.00	0.80[a]	0.21	0.57[a]	0.31	0.15	0.56[a]	0.49[a]	0.01	0.27
Acetaldehyde (2)		1.00	0.48[a]	0.52[a]	0.55[a]	0.17	0.70[a]	0.27	0.15	0.39
Acetone (3)			1.00	0.24	0.19	0.35	0.52[a]	0.08	0.56[a]	0.46[a]
Propionaldehyde (4)				1.00	0.28	0.55[a]	0.61[a]	0.49[a]	0.02	0.55[a]
Benzaldehyde (5)					1.00	0.10	0.29	−0.05	−0.11	0.17
Valeraldehyde (6)						1.00	0.49[a]	0.68[a]	0.07	0.86[a]
m-Tolualdehyde (7)							1.00	0.42[a]	0.11	0.55[a]
Hexaldehyde (8)								1.00	−0.20	0.65[a]
MEK (9)									1.00	0.03
Butyraldehyde (10)										1.00

[a]99% confidence levels.

Table 6
Correlations of carbonyl compounds at HKPU roadside station during winter intensive sampling

Compounds	1	2	3	4	5	6	7	8	9	10
Formaldehyde (1)	1.00	0.86[a]	−0.63	0.81[a]	0.90[a]	0.94[a]	0.66	0.85[a]	0.79[a]	0.93[a]
Acetaldehyde (2)		1.00	−0.57	0.87[a]	0.95[a]	0.76[a]	0.67	0.72	0.66	0.85[a]
Acetone (3)			1.00	−0.46	−0.59	−0.60	−0.65	−0.73	−0.54	−0.65
Propionaldehyde (4)				1.00	0.89[a]	0.69	0.63	0.55	0.50	0.76[a]
Benzaldehyde (5)					1.00	0.84[a]	0.73	0.72	0.59	0.86[a]
Valeraldehyde (6)						1.00	0.47	0.77[a]	0.81[a]	0.78[a]
m-Tolualdehyde (7)							1.00	0.75[a]	0.21	0.82[a]
Hexaldehyde (8)								1.00	0.74[a]	0.87[a]
MEK (9)									1.00	0.67
Butyraldehyde (10)										1.00

[a]99% confidence levels.

3.5. Comparison among three TAPs monitoring stations

Due to the differences in commercial, industrial and residential land uses in urban and suburban areas of Hong Kong, it is worthwhile to compare the levels of carbonyls from a vehicle dominated HKPU station with two TAP monitoring stations (CW and TW) operated by HKEPD. Monthly average concentrations of carbonyl species collected during the same period (April 1999–April 2000) were used for comparison.

As shown in Table 7, the annual average concentrations of carbonyls (e.g. formaldehyde = 5.25 μg/m^3 and acetaldehyde = 2.53 μg/m^3) detected at TW station were higher than the other two stations. But the differences of the concentrations among the three monitoring stations were relatively small in the range of 10–30%. The major source of carbonyl compounds were on-road vehicles. However, at TW station, industrial emissions were also one of the main sources for carbonyl compounds in addition to vehicle exhaust. Most carbonyl concentrations at HKPU station were higher than that at CW station. It was because the traffic flow near CW station was much less than that at HKPU. The high concentrations of formaldehyde, acetaldehyde and acetone at CW came from both anthropogenic and biogenic emissions (Singh et al., 1994, 1995).

Table 7
Average carbonyl concentrations of three monitoring stations

Compounds	HKPU (μg/m^3)	CW (μg/m^3)	TW (μg/m^3)
Formaldehyde	4.13	4.53	5.27
Acetaldehyde	2.01	1.73	2.53
Acetone	1.43	1.34	1.14
Propionaldehyde	0.24	0.26	0.48
Benzaldehyde	1.06	0.50	1.15
Valeraldehyde	0.24	0.16	0.25
m-Tolualdehyde	0.11	0.26	0.25
Hexaldehyde	0.89	0.23	0.37
MEK	0.42	0.34	1.19
Butyraldehyde	0.15	0.16	0.23

Summer to winter carbonyls ratios at CW and TW were listed in Table 8. Most ratios at CW and TW station were <1, which means the concentrations of carbonyls were higher in winter than those in summer.

Table 8
S/W of carbonyl compounds at CW and TW stations

Compounds	CW	TW
Formaldehyde	0.98	1.18
Acetaldehyde	0.69	0.87
Acetone	0.43	0.65
Propionaldehyde	0.36	0.63
Benzaldehyde	0.47	0.98
Valeraldehyde	0.40	0.37
m-Tolualdehyde	4.57	4.62
Hexaldehyde	0.80	1.07
MEK	0.43	2.76
Butyraldehyde	0.49	0.46

The variations were due to the distance between the source and the receptor. There was longer reaction time for the photolysis of secondary carbonyls at the TAP stations (CW and TW). Also, the effective dispersion of pollutants in summertime accounts for the lower summer/winter carbonyls ratios at CW and TW. However, the ratio of *m*-tolualdehyde at CW and the ratios of formaldehyde, *m*-tolualdehyde, hexaldehyde and MEK at TW were >1. These might be due to higher emissions of those compounds from other sources during summertime, especially the industrial emissions at TW.

4. Conclusion

The concentrations of carbonyl compounds were determined at HKPU station during the one-year monitoring from April 1999 to April 2000. Ten carbonyl species were identified and quantified. The most abundant carbonyl was formaldehyde ($4.13\,\mu g/m^3$). Most carbonyls have higher concentrations in summer than in winter. It was because photooxidation is an important source of carbonyls in summer other than primary emissions from vehicular exhaust. The main sources of carbonyls at HKPU station came from vehicle exhaust, especially in wintertime. The formaldehyde/acetaldehyde ratio (2.05) was similar to other urban areas and strong correlations of carbonyls in wintertime indicated that most carbonyls were from the same sources. Direct vehicular emissions were their principal source in winter at HKPU station. When compared with two other HKEPD TAPs monitoring stations, TW was found to have highest average carbonyl concentrations. It might be due to the addition of industrial emission from the nearby industrial area. Most summer/winter ratios at rooftop stations (CW and TW) were <1. The variations were due to the long distance between the source and the receptor and there was enough reaction time for the photolysis of secondary carbonyls. Also, the effective dispersion of pollutants in summer account for the lower summer/winter carbonyls ratios at CW and TW. In order to have a better understanding of primary and secondary sources of carbonyls, experiments for diurnal variations are in progress.

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