

# The pollution status of atmospheric carbonyls in a highly industrialized area

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## Abstract

The concentrations of 12 carbonyls in ambient air were measured from multiple locations of an urban area in the surroundings of a large industrial complex (August 2004 to September 2005). According to our field study, acetaldehyde ( $19.5 \pm 10.6$  ppb) and formaldehyde ( $19.3 \pm 10.1$  ppb) were found to be the two most abundant species followed by propionaldehyde ( $19.0 \pm 23.2$  ppb), acetone ( $15.9 \pm 15.2$  ppb) and butyraldehyde ( $13.0 \pm 19.8$  ppb). An examination of spatial variation patterns of carbonyls, when compared between industrial sites versus non-industrial sites, indicates that the mean values for each site type are statistically insignificant in most cases. In contrast, a comparison of temporal variation patterns indicates a fairly distinctive trend with the relative enhancement during summer (over winter) and/or daytime (over nighttime). The computation of the concentration ratios between some indicative species (e.g., formaldehyde/acetaldehyde and acetaldehyde/propionaldehyde) is unique enough to describe the pollution status of carbonyl species in the study area. Moreover, the relative contribution of several offensive odorous components (e.g., acetaldehyde, propionaldehyde, and butyraldehyde) is fairly strong, while their emissions are suspected to come from a substantial use of ethanol. The results of the present study thus confirm that the acquisition of ambient carbonyl concentration data is fairly useful for distinguishing the pollution status and the associated odor-related impacts.

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**Keywords:** Carbonyl compound; Ambient air; Urban environment

## 1. Introduction

As ubiquitous components in the atmosphere, carbonyls (aldehydes and ketones) have received immense attention due to their adverse health effects on humans and to their role as the major contributors to urban photochemical smog [1]. These compounds tend to be emitted directly from primary source processes such as exhaust gases of motor vehicles [2], incomplete combustion of hydrocarbon fuels in industrial processes [3,4], biomass burning [2], and urban incinerators [5]. Moreover, they are also released as the result of such secondary source processes as the photochemical oxidation of atmospheric hydrocarbons [3,4,6–11].

The environmental toxicity of carbonyls has been a primary scientific subject for various disciplines due to its common toxic effects of skin and eye irritation, nasopharyngeal membranes, carcinogenicity, etc. [4,12–17]. The short chain aldehydes have

been long known to exert a great impact on human health because of their potentially carcinogenic and mutagenic properties and their capacity for forming toxic and phytotoxic radical intermediates and stable species [2]. Hence, several carbonyls such as formaldehyde, acetaldehyde, and propionaldehyde have been included in a list of air toxins, e.g., the Clean Air Act Amendments of US EPA in the 1990s (e.g., ref. [4]). Considering the critical importance of carbonyls in atmospheric photochemistry, many efforts have been directed to the accurate assessment of their environmental behavior over a wide range of temporal and spatial scales.

In order to develop efficient air pollution abatement strategies toward its control, malodor regulation has been established in many countries by legislatively allocating offensive odorous components and their permissible ranges. In the case of Korea, five carbonyl compounds (e.g., acetaldehyde, propionaldehyde, butyraldehyde, valeraldehyde and isovaleraldehyde) have been selected among 12 offensive odorous pollutants since 2005 [18]. Hence, the concentration levels of carbonyls have been considered the critical part of the quantitative diagnosis of malodor emission.

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In an effort to comply with the social and environmental demand to resolve odor-related problems, we intended to diagnose the pollution level of carbonyl compounds in a large industrial complex area. As part of such efforts, the emission concentrations of carbonyls were investigated from diverse industrial source processes in our previous study [19]. In the course of the present study, we undertook the determination of ambient concentration levels of carbonyls in various locations of the urban area. These measurement data were then analyzed with respect to their relative composition and malodor intensity in relation with their spatial (e.g., industrial and non-industrial area) and temporal characteristics.

## 2. Materials and methods

### 2.1. Site characteristics

General information concerning the characteristics of the selected sampling locations throughout this study is described

in Table 1A. The determination of odorous compounds has been taken from various locations in the two neighboring cities of An San and Shi Hung (Gyung Gi province), Korea, which surround the Ban-Wall and Si-Hwa Industrial Complex (BW/SH IC), respectively (Fig. 1). The industrial complex was established in 1975 on the western side of the city directly facing the western coastline of Korea. Afterwards, a large residential area mainly consisting of high-altitude apartment buildings was built on the eastern side of the city in the 1990s. Because of the combined effects of geographical and meteorological conditions (e.g., prevalence of westerlies and oceanic winds), the residential area located in a downwind position is apt to suffer intensively and frequently from odor problems. Aiming to develop plans to relieve malodor problems in the target area, we have been involved in a number of projects to investigate sources of odors by determining their emission concentration levels [19,20]. In the present study, we intended to focus exclusively on the determination of carbonyl compounds in the ambient air surrounding the large industrial area.

Table 1

Basic information on sample acquisition in the present study; a total of 6 individual experiments were made from 10 sampling points during August 2004 to September 2005

(A) The location of 14 individual measurement sites investigated in this study

Order	Study site	Site ID	Site type <sup>a</sup>
1	Entrance area of industrial complex	A-1	I
2	Apartment area X	A-2	N
3	Bus stop	A-3	N
4	Church	A-4	N
5	Park	A-5	I
6	Middle school	A-6	N
7	Air product facility	A-7	I
8	Apartment area Y	A-8	N
9	Drug manufacturing facility	A-9	I
10	Paper company	A-10	I
11	Central Road (A)	B-1	N
12	Central Road (B)	B-2	N
13	Shoreline area	B-3	I
14	Light bulb manufacturing facility	B-4	N

(B) Basic environmental conditions of each field study

Order	Experiment number	Study period	Time of sampling		Target area	Temperature (°C)	RH (%)
			Season	Day/night			
1	P-I	August 11, 2004	Summer	Night	A-1 to A-10	31.9 ± 1.53 [31.8] <sup>b</sup> 29.9–34.4 [10] <sup>c</sup>	55.0 ± 5.45 [55.1] 47.8–66.0 [10]
2	P-II	August 12, 2004	Summer	Day	A-1 to A-10	31.2 ± 2.20 [32.0] 27.9–33.7 [10]	54.2 ± 9.68 [52.0] 44.0–70.0 [10]
3	P-III	January 11, 2005	Winter	Night	A-1, 2, 3, 5, 9, 10 B-1 to B-4	0.54 ± 2.40 [0.54] –2.80–5.00 [10]	39.1 ± 6.58 [39.1] 32.0–52.8 [10]
4	P-IV	July 27, 2005	Summer	Night	A-1, 2, 3, 5, 9, 10 B-1 to B-4	28.5 ± 0.86 [28.6] 26.7–29.9 [10]	70.0 ± 4.14 [70.0] 64.9–76.8 [10]
5	P-V	August 4, 2005	Summer	Day	A-1, 2, 3, 5, 9, 10 B-1 to B-4	33.8 ± 1.92 [33.3] 30.8–36.6 [10]	55.4 ± 9.41 [54.6] 40.3–70.0 [10]
6	P-VI	September 27, 2005	Fall	Night	A-1, 2, 3, 5, 9, 10 B-1 to B-4	29.1 ± 2.15 [29.3] 26.4–33.0 [10]	34.9 ± 5.80 [34.3] 25.2–45.4 [10]

<sup>a</sup> I, Industrial; N, non-industrial.

<sup>b</sup> Median.

<sup>c</sup> Number of sample.

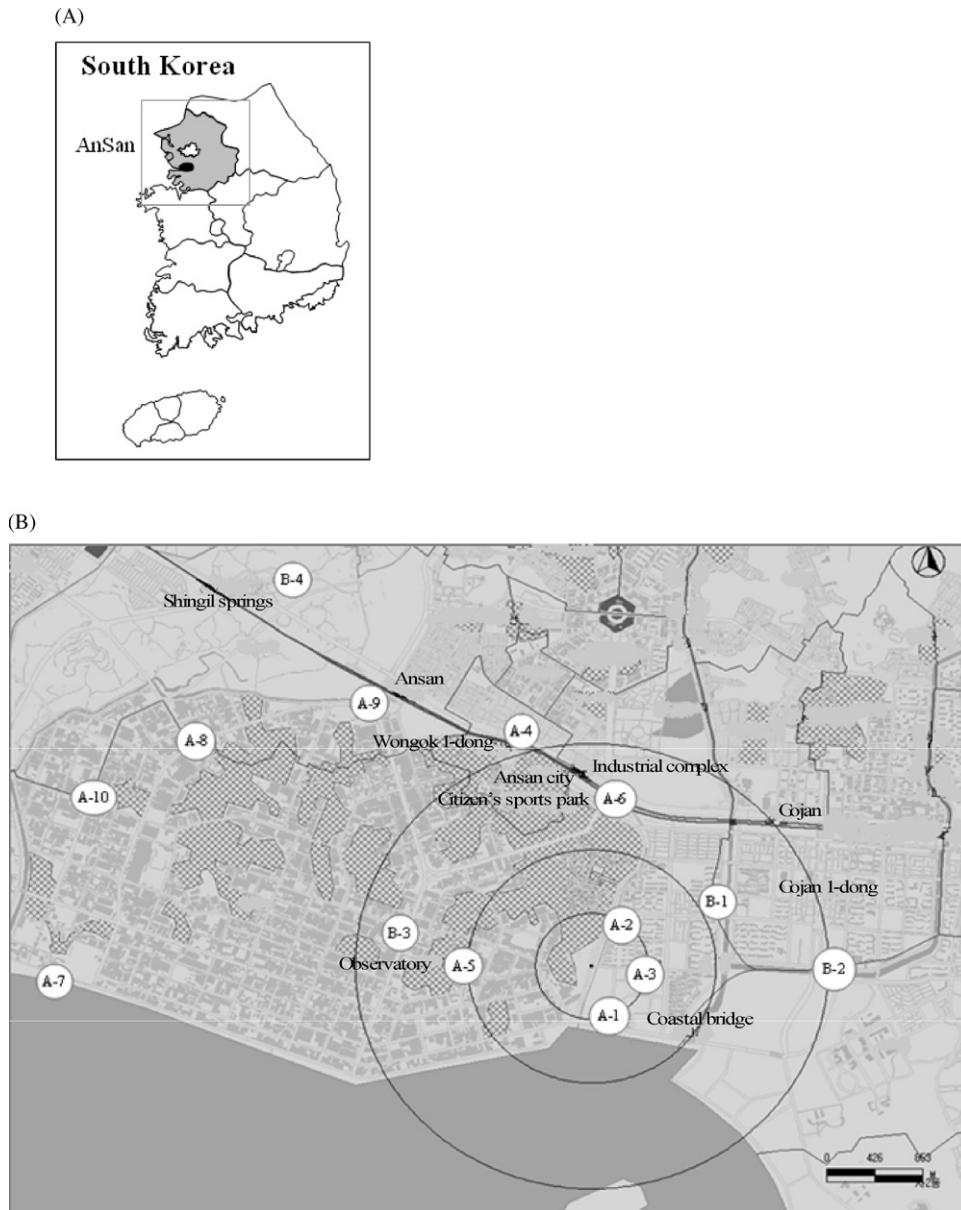


Fig. 1. Geographical location of the study site. (A) Ansan city, South Korea and (B) sampling site.

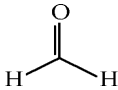
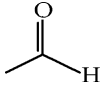
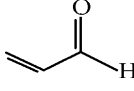

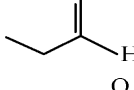
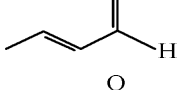
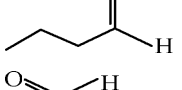
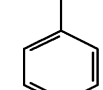
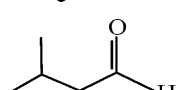
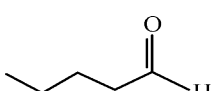
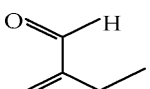
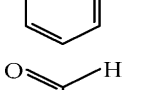
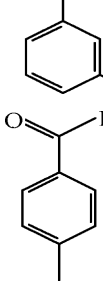
As part of this project, the concentrations of important odorous compounds have been measured from a total of 6 field campaigns each of which covers 10 sampling points during August 2004 to September 2005 (Fig. 1B). In the early part of our field study (Period I (August 11, 2004: nighttime) and II (August 12, 2004: daytime)), all samples were taken from the following 10 locations: [1] entrance area of the industrial complex (A-1), [2] apartment area X (A-2), [3] bus stop (A-3), [4] church (A-4), [5] park (A-5), [6] middle school (A-6), [7] air product facility (A-7), [8] apartment area Y (A-8), [9] drug manufacturing facility (A-9) and [10] paper company (A-10). However, in the later part of our field study (Period III (November 01, 2005: nighttime), IV (July 27, 2005: nighttime), V (August 04, 2005: daytime) and VI (September 27, 2005: nighttime)), four of these sampling points (A-4, A-6, A-7 and A-8) had been replaced with new positions. All of the location codes for the newly selected

sampling points were then assigned with the capital letter B as in the following: central road A (B-1), central road B (B-2), shoreline area (B-3), and near light bulb manufacturing facility (B-4). Out of these 14 sampling sites, 6 were positioned in the industrial region (e.g., A-1, A-5, A-7, A-9, A-10, and B-3), whilst 8 were in a non-industrial locale (e.g., A-2, A-3, A-4, A-6, A-8, B-1, B-2, and B-4). The collection of carbonyl samples was made from 10 individual locations within the study area during six field studies (Period (P)-I through VI). Information concerning the basic environmental conditions (temperature and relative humidity (RH)) was recorded routinely during each sampling (Table 1B).

## 2.2. Sample collection

In the present study, samples were collected and analyzed to measure up to 12 carbonyl compounds (Table 2); five of

Table 2  
A list of carbonyl compounds investigated in this study

Order	Name of carbonyl		Molecular formula	Molecular weight	Chemical structure
	Full	Short			
1	Formaldehyde	Form-A	HCHO	30.03	
2	Acetaldehyde <sup>a</sup>	Acet-A	CH <sub>3</sub> CHO	44.05	
3	Acrolein	Acrolein	CH <sub>2</sub> CHCHO	56.06	
4	Acetone	Acetone	CH <sub>3</sub> COCH <sub>3</sub>	58.08	
5	Propionaldehyde <sup>a</sup>	Propion-A	CH <sub>3</sub> CH <sub>2</sub> CHO	58.08	
6	Crotonaldehyde	Croton-A	CH <sub>3</sub> CHCHCHO	70.09	
7	Butyraldehyde <sup>a</sup>	Butyr-A	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CHO	72.11	
8	Benzaldehyde	Benz-A	C <sub>6</sub> H <sub>5</sub> CHO	106.12	
9	Isovaleraldehyde <sup>a</sup>	Isovaler-A	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CHO	86.13	
10	Valeraldehyde <sup>a</sup>	Valer-A	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CHO	86.13	
11	<i>o</i> -Tolualdehyde	<i>o</i> -Tolu-A	CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CHO	120.15	
12	<i>m</i> -Tolualdehyde	<i>m</i> -Tolu-A	CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CHO	120.15	
13	<i>p</i> -Tolualdehyde	<i>p</i> -Tolu-A	CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CHO	120.15	

<sup>a</sup> Offensive odorous carbonyls assigned by KMOE.

those belong to the sum of 12 offensive odorous pollutants established by the KMOE [18]. The air samples were passed through Lp DNPH cartridges (Supelco Inc., USA) at variable sampling conditions at the field site. Sampling duration was basically made at a normal set-up value of 15 min (at a fixed sampling flow rate of 1 L min<sup>-1</sup>). During each sampling, a Sep-Pak ozone scrubber (Waters, USA) was placed upstream of the cartridge to avoid artifact interferences such as the degradation of carbonyl-hydrazones [1]. The sampled cartridges were then wrapped in aluminum foil, transported immediately to the laboratory, and stored in a refrigerator until analysis (normally within 24 h). In most cases, one laboratory blank and one field blank were reserved for analysis each day during sampling.

### 2.3. Carbonyl analysis

The carbonyl-hydrazones were analyzed by HPLC (Lab Alliance 500) equipped with a UV detector and dsCHROM software for peak integration. To initiate the analysis, the sampled cartridges were eluted slowly with acetonitrile in a 5 mL capacity borosilicate glass volumetric flask. The eluate was injected in the HPLC system equipped with a 20  $\mu$ L sample loop. Different carbonyl-hydrazones were separated on a Hichrom 250 mm  $\times$  4.6 mm ODS, 5  $\mu$ m RP C<sub>18</sub> column using a mobile phase of acetonitrile + water (6.5:3.5, v/v) at a flow rate of 1.5 mL min<sup>-1</sup>. The detection of all carbonyl-hydrazones was then made at a wavelength of 360 nm. For the quantification of carbonyls, a five-point calibration was conducted by injecting 20  $\mu$ L of liquid phase standards made of carbonyl-DNPH Mix (Supelco, USA) at 0.05, 0.1, 0.3, 0.6 and 1.0 ng  $\mu$ L<sup>-1</sup>. The solvents used in this study were all of HPLC grade.

The basic quality assurance (QA) of our experimental method can be assessed in terms of such analytical parameters as limit of detection (LOD) and precision. As discussed in our recent publication (e.g., ref. [19]), the LOD values for all of the carbonyl species were estimated by multiplying the standard deviation (S.D.) values of the least detectable quantities (in absolute mass or concentration unit) by a factor of 3. The LOD values, if expressed in terms of mixing ratio (assuming a total sampling volume of 15 L), were found to fall in the range of 0.07 (crotonaldehyde) to 0.09 ppb (formaldehyde). In addition, the precision of analysis, when assessed in terms of the RSE value of triplicate analyses, tended to vary in the range of 0.53 (formaldehyde) to 1.45% (*p*-tolualdehyde).

## 3. Results and discussions

### 3.1. Carbonyls in the ambient air in the surroundings of the industrial area

In this study, we originally attempted to quantify up to a total of 13 carbonyl compounds as listed in Table 2. They can be classified into seven saturated aliphatic carbonyls (formaldehyde, acetaldehyde, acetone, propionaldehyde, butyraldehyde, isovaleraldehyde, and valeraldehyde), two unsaturated aliphatic carbonyls (acrolein and crotonaldehyde), and four aromatic carbonyls in the samples (benzaldehyde,

*o*-tolualdehyde, *m*-tolualdehyde, and *p*-tolualdehyde). Interestingly, *o*-tolualdehyde was highly unique in that it was not detected in all the ambient air samples. In addition, acrolein and *m*-tolualdehyde were detected in only one and two samples, respectively. Hence, all of our measurements were actually made for the remaining 12 carbonyl compounds. The basic physico-chemical properties (e.g., molecular formula, molecular weight and chemical structure) of the 12 identified carbonyls are presented in Table 2 along with *o*-tolualdehyde (not quantified in this study). To simplify the comparison between carbonyls, we henceforth will use the short names as introduced in Table 2.

A statistical summary of the carbonyls detected during the entire study period (August 2004 to September 2005) is presented in Table 3. Most of the aliphatic carbonyls (e.g., Form-A, Acet-A, Acetone, Propion-A, and Butyr-A) are found to be very abundant. However, some others (Acrolein, Croton-A, Isovaler-A, and Valer-A) were only occasionally detected in few samples with very low concentration. Among the aromatic carbonyls, Benz-A is profuse in the studied samples, while *m*-Tolu-A and *p*-Tolu-A are scarce. The results show that the absolute magnitude of carbonyls, when compared in terms of mean concentration (ppb), is found in the descending order of Acet-A (19.5), Form-A (19.3), Propion-A (19.0), Acetone (15.9), Butyr-A (13.0), Benz-A (4.79), *p*-Tolu-A (3.60), Croton-A (1.62), Acrolein (1.44), Isovaler-A (0.93), Valer-A (0.82) and *m*-Tolu-A (0.47). As a result, Acet-A is found as the most abundant carbonyl in the present study. This result contrasts with the previous studies in that Form-A is the most abundant ambient carbonyl in many countries (e.g., Italy [17]; China [14]; Japan [5]; Canada [21]; and USA [4]). However, when we consider the median values (in ppb unit) for such comparison, the slightly different trend is observed: Form-A (20.6), Acet-A (15.7), Propion-A (15.0), Acetone (13.5), Butyr-A (5.42), Benz-A (2.34), Acrolein (1.44), Croton-A (1.42), *p*-Tolu-A (1.34), Isovaler-A (1.00), Valer-A (0.77) and *m*-Tolu-A (0.47). Considering both comparative criteria, Form-A and Acet-A can be regarded as the most abundant carbonyls in the environment. It is also noted that most of carbonyls generally exhibit fairly strong variabilities as shown by the coefficient of variation (CV) values (%), in the descending order of Butyr-A (152), Benz-A (150), *p*-Tolu-A (127), Propion-A (122), Croton-A (109), Acetone (95.9), Isovaler-A (59.7), *m*-Tolu-A (56.3), Acet-A (54.0), Form-A (52.1) and Valer-A (45.4).

### 3.2. Temporal, spatial, and seasonal patterns in carbonyl distribution in the present study

The absolute concentration data of all carbonyls measured in the present study have been grouped into different categories (Table 4) to describe diurnal (e.g., daytime versus nighttime), seasonal (e.g., summer, fall, winter) and spatial variation patterns (e.g., industrial versus non-industrial sites). If we compare the present dataset in terms of diurnal variations, higher concentrations were generally found in the daytime samples such as Form-A, Acet-A, Acetone, Propion-A and Isovaler-A (with some exceptions of Butyr-A, Benz-A, Valer-A and *p*-Tolu-a) (Table 4A). Four out of five cases, showing relative dominance

Table 3

A statistical summary of carbonyl concentrations in ambient air determined during the entire study period

Order	Carbonyl compounds <sup>a</sup>	Concentration (ppb)						
		Mean	Median	S.D. <sup>b</sup>	CV <sup>c</sup>	Minimum	Maximum	N <sup>d</sup>
1	Form-A	19.3	20.6	10.1	52.1	2.15	42.2	60 (60 <sup>e</sup> )
2	Acet-A	19.5	15.7	10.6	54.0	5.94	46.8	60 (60)
3	Acrolein	1.44	1.44	–	–	1.44	1.44	60 (1)
4	Acetone	15.9	13.5	15.2	95.9	0.64	96.9	60 (59)
5	Propion-A	19.0	15.0	23.2	122	1.43	166	60 (60)
6	Croton-A	1.62	1.42	1.77	109	0.07	5.58	60 (8)
7	Butyr-A	13.0	5.42	19.8	152	0.08	120	60 (57)
8	Benz-A	4.79	2.34	7.16	150	0.20	36.4	60 (47)
9	Isovaler-A	0.93	1.00	0.55	59.7	0.10	1.71	60 (13)
10	Valer-A	0.82	0.77	0.37	45.4	0.23	1.68	60 (13)
11	<i>m</i> -Tolu-A	0.47	0.47	0.26	56.3	0.28	0.65	60 (2)
12	<i>p</i> -Tolu-A	3.60	1.34	4.59	127	0.37	12.7	60 (13)

<sup>a</sup> Refer to Table 2 for the full information of each carbonyl compound.<sup>b</sup> Standard deviation.<sup>c</sup> Coefficient of variation.<sup>d</sup> Number of sample.<sup>e</sup> The concentration data falling in the valid concentration range (i.e., above limit of detection).

over the daytime, were found to be statistically significant with an exception of acetone (Table 4D). The relative pattern of nighttime depletion, observed from several carbonyls (e.g., Form-A, Acet-A, Propion-A and Isovaler-A), is suspected to come from their susceptibility to the reactions with NO<sub>3</sub> radicals [6,22]. However, Acrolein, Croton-A and *m*-Tolu-A cannot be compared in this respect, as they were detected only in nighttime samples.

An inspection of the seasonal variation patterns indicates that the highest concentrations of most carbonyls were found in the summer samples with exceptions of Acet-A and Acetone (in fall) and Valer-A (in winter) (Table 4B). In the fall season, most of the carbonyls were quantified at or below LOD. Thus,

comparison of the seasonal pattern was made between the data sets of summer and winter seasons. The results showed that out of the nine cases, eight matching pairs (e.g., Form-A, Acet-A, Acetone, Propion-A, Croton-A, Butyr-A, Benz-A, and Isovaler-A) showed more enhanced values during the summer than the winter season with a single exception of Valer-A. In four of those eight cases, the differences were statistically significant (e.g., at  $P < 0.01$ ) as follows: Form-A, Acetone, Butyr-A and Isovaler-A (Table 4D). Higher ambient temperature and strong solar radiation during summer may have facilitated the photochemical reactions generating aldehydes, while also accelerating the photolysis of secondary aldehydes to form hydroxy radicals. Therefore, the net carbonyls content will be governed by

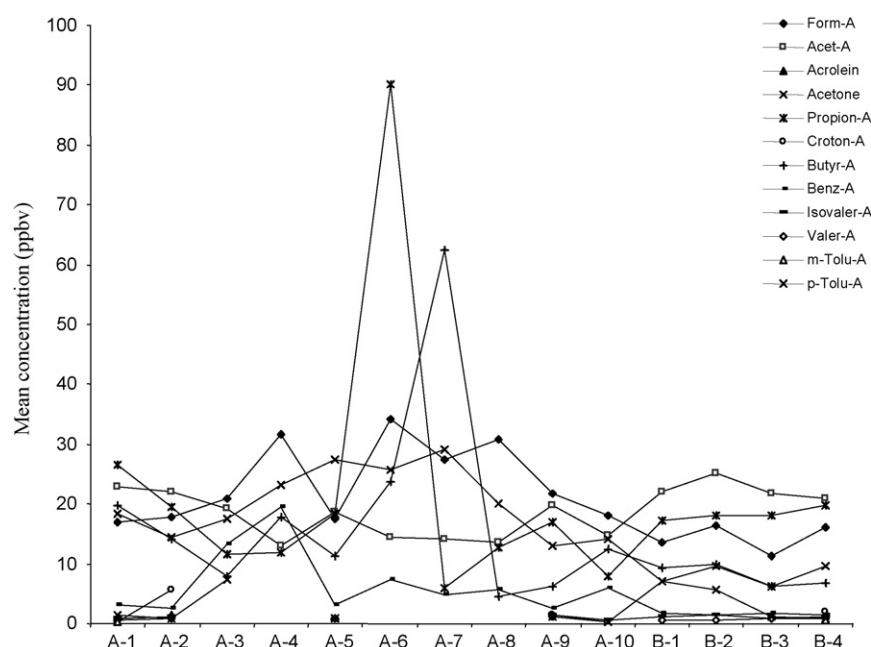


Fig. 2. Comparison of the arithmetic mean concentration levels of ambient carbonyls measured in each sampling point from a total of six field campaigns.



Table 4

A statistical summary of carbonyl concentrations in ambient air in terms of three classification criteria: site characteristics, diurnal and seasonal variations

## (A) Comparison of concentration data in terms of diurnal variation

Order	Carbonyl compounds	Diurnal variation					
		Daytime			Nighttime		
		Mean	Median <sup>a</sup>	S.D. <sup>b</sup>	Mean	Median	S.D.
1	Form-A	24.0	24.3	6.88	16.9	13.6	10.6
2	Acet-A	23.1	16.6	13.3	17.8	15.4	8.53
3	Acrolein	–	–	–	1.44	1.44	–
4	Acetone	19.5	13.5	20.3	14.0	11.1	11.7
5	Propion-A	31.0	24.5	35.7	13.0	14.1	9.18
6	Croton-A	–	–	–	1.62	1.42	1.77
7	Butyr-A	11.2	7.54	7.78	14.0	4.92	24.0
8	Benz-A	3.98	1.96	5.04	5.17	2.39	8.01
9	Isovaler-A	1.22	1.28	0.35	0.26	0.27	0.21
10	Valer-A	0.76	0.77	0.16	0.92	1.01	0.60
11	<i>m</i> -Tolu-A	–	–	–	0.47	0.47	0.26
12	<i>p</i> -Tolu-A	1.22	1.08	0.66	11.5	11.8	1.34

## (B) Comparison of concentration data in terms of seasonal variation

Order	Carbonyl compounds	Seasonal variation								
		Summer			Fall			Winter		
		Mean	Median	S.D.	Mean	Median	S.D.	Mean	Median	S.D.
1	Form-A	21.4	23.8	10.6	20.3	21.0	6.15	9.82	9.78	3.98
2	Acet-A	18.5	14.6	10.7	29.4	29.7	5.42	14.0	12.4	7.53
3	Acrolein	1.44	1.44	–	–	–	–	–	–	–
4	Acetone	17.6	13.5	17.6	18.5	18.6	3.88	5.19	5.09	2.26
5	Propion-A	22.3	15.1	27.1	17.8	15.2	11.2	7.17	4.33	6.13
6	Croton-A	2.17	1.50	2.40	–	–	–	1.08	1.08	0.86
7	Butyr-A	17.5	7.54	22.9	5.82	4.92	3.97	2.71	2.08	2.30
8	Benz-A	6.35	3.30	8.77	2.15	2.08	0.43	2.37	2.34	1.58
9	Isovaler-A	0.97	1.05	0.56	–	–	–	0.44	0.44	–
10	Valer-A	0.70	0.76	0.23	–	–	–	1.10	1.14	0.52
11	<i>m</i> -Tolu-A	–	–	–	–	–	–	0.47	0.47	0.26
12	<i>p</i> -Tolu-A	3.60	1.34	4.59	–	–	–	–	–	–

## (C) Comparison of concentration data in terms of spatial variation

Order	Carbonyl compounds	Site characteristics					
		Industrial			Non-industrial		
		Mean	Median	S.D.	Mean	Median	S.D.
1	Form-A	18.2	17.2	10.1	20.4	21.6	10.1
2	Acet-A	19.0	16.5	10.2	20.1	15.4	11.0
3	Acrolein	–	–	–	1.44	1.44	–
4	Acetone	17.3	16.4	18.5	14.4	12.9	11.3
5	Propion-A	16.8	13.7	13.0	21.2	15.1	30.3
6	Croton-A	0.71	0.41	0.70	3.13	1.93	2.12
7	Butyr-A	14.9	5.39	24.9	10.9	5.42	12.0
8	Benz-A	3.42	2.91	3.43	6.34	2.25	9.70
9	Isovaler-A	0.81	0.75	0.60	1.11	1.09	0.45
10	Valer-A	0.82	0.77	0.47	0.83	0.75	0.27
11	<i>m</i> -Tolu-A	0.28	0.28	–	0.65	0.65	–
12	<i>p</i> -Tolu-A	0.99	1.01	0.42	5.23	2.18	5.30

## (D) Test of statistical significance in terms of site characteristics, diurnal and seasonal variations

Order	Carbonyl compound	<i>p</i> -Value			<i>t</i> -Value		
		D/N <sup>c</sup>	S/W <sup>d</sup>	Site <sup>e</sup>	D/N	S/W	Site
1	Form-A	0.009	0.002	0.410	99.1	99.9	59.0
2	Acet-A	0.065	0.216	0.717	93.5	78.4	28.3

Table 4 (Continued)

Order	Carbonyl compound	<i>p</i> -Value			<i>t</i> -Value		
		D/N <sup>c</sup>	S/W <sup>d</sup>	Site <sup>e</sup>	D/N	S/W	Site
3	Acroelin	–	–	–	–	–	–
4	Acetone	0.186	0.041	0.475	81.4	95.9	52.5
5	Propion-A	0.039	0.106	0.467	96.1	89.4	53.3
6	Croton-A	–	0.425	0.050	–	57.5	95.0
7	Butyr-A	0.610	0.050	0.450	39.0	95.0	55.0
8	Benz-A	0.601	0.188	0.165	39.9	81.2	83.5
9	Isovaler-A	0.0004	–	0.359	100	–	64.1
10	Valer-A	0.480	0.072	0.964	52.0	92.8	3.58
11	<i>m</i> -Tolu-A	–	–	–	–	–	–
12	<i>p</i> -Tolu-A	–	–	0.107	100	–	89.3

Footnotes 'a' through 'b' denote median and standard deviation, respectively, and 'c' through 'e' denote daytime vs. nighttime, summer vs. winter and industrial vs. non-industrial site, respectively.

the equilibrium between the photochemical reactions producing aldehydes and the removal processes [16]. Photochemical reactions can account for 80–90% of the carbonyl concentrations in summer [10,13,23]. An increase in relative humidity during summer (compared to fall and winter (Table 1B)) might have led to the elevation of carbonyl concentrations by stimulating the formation of HNO<sub>2</sub> which then can initiate urban photochemistry [13,24].

To investigate the hot spot areas within our measurement locations, the occurrence patterns of the maximum carbonyl concentration were examined among different sampling points (Fig. 2). The maximum arithmetic mean concentrations for different carbonyls were commonly seen from such sites: A-2 [N] (Acrolein and Croton-A), A-7 [I] (Acetone and Butyr-A), A-9 [I] (Valer-A and Isovaler-A) and so on. In contrast, the occurrence patterns of the minimum concentrations were found in other sites such as: A-1 [I] (Valer-A and *m*-Tolu-A), A-10 [I] (Isovaler-A and *p*-Tolu-A), B-3 [I] (Form-A and Acetone) and others. A simple comparison of the occurrence pattern between the maximum and minimum concentration data thus indicates that the grouping of site types between industrial and non-industrial areas is not necessarily an effective tool to distinguish their spatial patterns.

If we inspect the spatial distribution of each carbonyl compound, then the highest concentration of Form-A (34.3 ppb) was observed in the A-6 site and the lowest (11.2 ppb) in the B-3 site (Fig. 2). The samples from A-6 site were drawn in the Periods I and II during summer seasons. It may thus be possible to infer that higher ambient temperatures in summer might have promoted the photochemical reactions for the production of aldehydes (e.g., ref. [16]). The possibly important role of such reaction may be further supported by the presence of a statistically significant correlation between the Form-A concentration and ambient temperature ( $P < 0.01$ ,  $r = 0.50$ ) (Table 5).

Likewise, an inverse correlation was also recognized between Form-A and the relative humidity ( $r = -0.14$ ) (Table 5). Our result thus appears to corroborate well with the previous findings from the Rome [25] and Eastern Finland [11] in that maximum levels of Form-A were observed during summer. It is however suspected that the lowest value of Form-A in the B-3 site is due to the dilution effect in the shoreline area.

According to our inspection of the spatial distribution between different carbonyls, relatively enhanced concentrations of carbonyls are generally observed from the non-industrial sites (Table 4C). The only exceptions from such patterns were seen in the case of Acetone and Butyr-A. However, according to the *t*-test, the differences between the two site types were found to be statistically insignificant with only a single exception (i.e., Croton-A) (Table 4D). Thus, consideration of site-type characteristics between industrial and non-industrial locations in the present study is unlikely to be critical relative to such a criterion as temporal factors. Previous studies from other cities in the world (as listed in Table 6) however showed much higher concentrations for most of the carbonyls in the ambient air of industrial sites relative to the background urban air, as discussed below.

### 3.3. Comparison of carbonyls between different studies

A great number of studies have been conducted in different parts of the world to measure ambient levels of carbonyls in urban and rural atmospheres: USA (e.g., refs. [4,26]), Canada (e.g., ref. [21]), Brazil (e.g., refs. [3,9,27–29]), Chile (e.g., ref. [30]), Mexico (e.g., refs. [7,8]), Denmark (e.g., ref. [22]), Greece (e.g., ref. [1]), France (e.g., ref. [31]), China (e.g., refs. [13,14,16,32,33]), Japan (e.g., ref. [34]), Lebanon (e.g., ref. [6]), Egypt (e.g., ref. [35]), etc. For a better insight into the dis-

Table 5  
Correlation of carbonyls with the ambient temperature and relative humidity (RH)

	Form-A	Acet-A	Acetone	Propion-A	Croton-A	Butyr-A	Benz-A	Isovaler-A	Valer-A	<i>p</i> -Tolu-A
Temperature	<u>0.50</u>	0.28	0.32	0.24	0.30	0.26	0.20	<u>0.47</u>	<u>-0.50</u>	<u>-0.82</u>
RH	-0.14	-0.26	-0.12	0.11	<u>0.40</u>	0.18	0.11	<u>-0.39</u>	-0.14	<u>0.66</u>

Statistically significant values at  $P < 0.01$  level of significance have been underlined.



Table 6  
Comparison of absolute carbonyl measurement data (in ppb) reported from the present and previous studies

Site characteristics	Reference	Country	Study site	Study period	Carbonyl compound													
					Form-A	Acet-A	Acrolein	Acetone	Propion-A	Croton-A	Butyr-A	Benz-A	Isovaler-A	Valer-A	o-Tolu-A	m-Tolu-A	p-Tolu-A	
Ambient air (industrial)	Present study	S. Korea	Banwall	2004–2005	19.3	19.5	1.44	15.9	19.0	1.62	13.0	4.79	0.93	0.82	–	–	–	–
	[17]	Italy	Boffalora	1998–1999	6.12	2.50	–	–	0.84	0.18	0.42	0.12	–	0.14	–	–	–	–
	[14]	China	Guangzhou	2003	11.5	4.10	–	9.31	0.57	0.14	0.31	0.17	0.08	0.64	0.37	–	–	–
	[5]	Japan	Osaka	2003	3.77	1.42	0.01	3.40	0.20	0.01	0.09	0.16	0.06	0.05	–	–	–	–
	[21]	Canada	Urban area	2003–2005	1.94	0.89	0.04	1.62	0.16	0.02	–	0.04	0.03	0.06	0.01	–	–	–
Urban background air	[4]	USA	Elizabeth city	1999–2001	5.32	4.83	0.58	1.59	0.54	0.13	–	0.37	–	–	–	–	–	–
	[9]	Brazil	Rio de Janeiro	2000	9.92	5.52	0.33	1.93	0.42	0.10	0.16	0.24	0.07	0.07	0.01	–	–	–
	[8]	Mexico	Mexico city	1996	26.1	15.6	–	11.81	3.21	–	3.18	–	–	–	–	–	–	–
	[7]	Mexico	Xalapa city	1997	3.0	11.6	–	–	–	–	–	–	–	–	–	–	–	–
	[16]	China	Urban area	1997–2000	3.62	1.19	–	0.56	0.18	0.04	0.06	0.13	0.03	0.07	0.03	0.10	–	–

Conversion from  $\mu\text{g m}^{-3}$  to ppbv is made assuming  $P = 1 \text{ atm}$ ;  $T = 298 \text{ K}$ ;  $R = 0.08208 \text{ L atm mol}^{-1} \text{ K}^{-1}$  except for the ref. [7].

tribution characteristics of carbonyls, our present dataset was compared with those measured under different environmental conditions (e.g., areas affected by industrial activities and background urban environments).

The absolute magnitudes of carbonyl concentration data measured from the present study are in general significantly higher than those seen from the other environments, as compiled in Table 6. However, the absolute arithmetic mean concentration of Form-A (19.3 ppb) in the present study is lower than that seen from the background area of Mexico (26.1 ppb) [8]; the Form-A data measured by Báez et al. [8] are in fact found to be the highest of all reported data, irrespective of site types (industrial or urban background air). The data available from the great deal of literature (Table 6) showed that the absolute concentrations of each carbonyl measured from the surroundings of the industrial environment (e.g., refs. [5,14,17]) are notably higher (e.g., by approximately an order of magnitude) than those measured from the background air [4,7–9,16,21]. It is however interesting to note that some of carbonyl concentration data measured at the industrial site of Italy [17] and Japan [5] are significantly low. In fact, they are even smaller than those reported from the background areas in Brazil [9] and Mexico [8].

### 3.4. Information concerning the relative composition of carbonyls

As a simple means to evaluate the occurrence patterns of each carbonyl compound, their relative ordering was compared using the datasets for the present study. It is quite striking to find that the relative distribution patterns of all different studies are fairly comparable with each other, regardless of differences in the environmental conditions encountered in each sampling site. The results of most studies consistently show that the dominant carbonyls are in the descending order of Acet-A, Form-A, Propion-A, Acetone, Butyr-A, Benz-A, and other minor components (Fig. 3). The relative composition of the five offensive odorous pollutants was compared further using the datasets of other studies as well (Table 7); the relative proportion of those five compounds measured in the present study are found to be substantially high compared to other parts of the world, regardless of location whether industrial or urban background areas.

As a simple means to assess the factors controlling the distributions of carbonyls, the concentration ratios between different carbonyls were evaluated by such combinations as  $C_1/C_2$  (Form-A/Acet-A) and  $C_2/C_3$  (Acet-A/Propion-A) (Table 7). Both concentration ratios determined in the present study are much lower than those of different countries, regardless of site types. The  $C_1/C_2$  ratio in the present study (e.g., mean for all data: 0.99) recorded the lowest value, while the highest value was observed in the urban background air in Hong Kong (3.04). The result of our study thus complies well with the common finding in that  $C_1/C_2$  normally varies from 1 to 2 in the polluted environment (e.g., urban areas) to about 10 in the clean background environment [1,14,25]. The mean  $C_1/C_2$  ratio (0.99) in the present study also complies well with the literature data (1.10) as reported from USA [4]. This observation indirectly supports the insignificant role of biogenic sources in the production

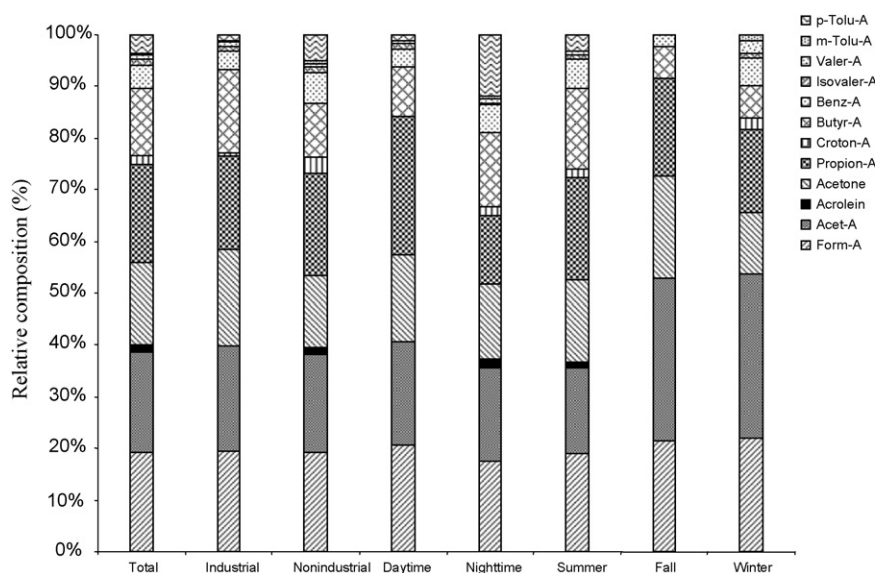


Fig. 3. Comparison of relative composition (%) of ambient carbonyl concentrations.

of Form-A in the study area [16]. The fairly reduced  $C_1/C_2$  ratio values (0.99) further suggest the possible use of ethanol containing fuels or chemicals in the Ban Wall industrial area. The lower  $C_1/C_2$  ratio values at night (0.95) compared to daytime (1.04) are compatible with theory in that Form-A exhibits the higher dry deposition velocity relative to Acet-A at night [13]. Moreover, because of the possible role of the secondary formation of aldehydes, the production of Acet-A during nighttime may significantly exceed that of Form-A [13]. The higher  $C_1/C_2$  ratio value during daytime (1.04) and/or summer (1.16) in the

present study may also be accounted for by the extended lifetime of Form-A compared to Acet-A with respect to photolysis and reactions with hydroxyl radicals,  $NO_3$  radical, and  $O_3$  [24]. The higher  $C_1/C_2$  ratio values in summer (1.16) compared to fall (0.69) and winter (0.70) in the present study also corroborates well with the previous report from Rome [25] and eastern Finland [11]; those studies also reported the existence of maximum Form-A levels in summer. This is further supported by the experimental estimation of the secondary conversion of alkenes to aldehydes in which the yields of Form-A and Acet-A in summer are 0.39 and 0.18, respectively, and 0.23 and 0.15, respectively, in winter [36]; this is also supported by some theoretical considerations (e.g., the reaction rate constants of Form-A by hydroxyl radicals) as reported previously [16,37]. However, considering the anthropogenic to biogenic factors, the  $C_1/C_2$  ratio should be used very carefully since the lifetime of Acet-A (with respect to photolysis and reaction with OH radical,  $NO_3$ , and  $O_3$ ) is substantially less compared to Form-A [24]. This factor can lead to changes in the  $C_1/C_2$  ratio depending upon the atmospheric chemistry under particular meteorological condition.

The  $C_2/C_3$  concentration ratio is also useful to indicate the measure of anthropogenic factors; this is because propionaldehyde is supposed to originate mainly from industrial emissions [25]. Thus,  $C_2/C_3$  values are generally found to be high in rural background air, while low in urban air [14]. The  $C_2/C_3$  ratio in the present study (e.g., all: 1.03) is the lowest of all, while the highest value is observed in the background area in Brazil (13.14). However, when we compare the  $C_2/C_3$  ratio value among all study sites, we generally found a slightly reduced value in the non-industrial sites (0.95) compared to the industrial site (1.13). The  $C_2/C_3$  ratio value is also low during daytime (0.75) compared to nighttime (1.37). However, in terms of the seasonal differences, the lowest value was observed during the summer (0.83), while much enhanced values were seen in the fall (1.65) and winter (1.95). The relatively reduced ratio values during daytime (0.75) and/or summer (0.83) are found to

Table 7

Relative composition (%) of five offensive odorous pollutants among all 13 carbonyl compounds and some important concentration ratios are compared between the present and previous studies

Reference	Relative sum of five carbonyls (%)	Concentration ratio	
		Form/Acet ( $C_1/C_2$ )	Acet/Prop ( $C_2/C_3$ )
<b>Present study</b>			
All data	53.1	0.99	1.03
Industrial site	56.1	0.96	1.13
Non-industrial site	51.2	1.02	0.95
Daytime	58.0	1.04	0.75
Nighttime	47.4	0.95	1.37
Summer	53.2	1.16	0.83
Fall	56.4	0.69	1.65
Winter	57.3	0.70	1.95
<b>Other studies</b>			
[17]	37.4	2.45	2.98
[14]	20.7	2.80	7.19
[5]	19.9	2.66	7.18
[21]	23.6	2.18	5.56
[4]	40.2	1.10	8.94
[9]	33.1	1.80	13.14
[8]	36.7	1.68	4.85
[7]	79.4	0.26	–
[16]	25.1	3.04	6.61

be persistent in spite of the higher lifetime for Acet-A compared to Propion-A with respect to photolysis and reactions with hydroxyl radicals, NO<sub>3</sub> radical and O<sub>3</sub> [24]. The large photochemical production of Acet-A under high temperatures and strong solar radiation may be counterbalanced by the rapid loss due to photolysis and reactions with hydroxyl radicals [16,22]. Therefore, the use of the C<sub>2</sub>/C<sub>3</sub> concentrations ratio values should be made cautiously in diagnosing the effects of anthropogenic source processes for the carbonyl pollution in air.

### 3.5. Factors controlling carbonyl concentrations

The factors controlling the absolute concentrations of carbonyls and their source processes have been assessed indirectly by means of correlation analysis in the present study. Correlation analysis has the potential to predict the movement in one variable relative to other. Considering the abundance of the dataset, the strength of correlations between nine carbonyls (e.g., Form-A, Acet-A, Acetone, Propion-A, Croton-A, Butyr-A, Benz-A, Isovaler-A and Valer-A) has been examined for statistical significance at  $P < 0.01$  level (Table 8A). The cases of strongly correlated pairs were observed from 20 out of all (44) matching cases. Moreover, out of those 20 significant cases, a total of 6 cases showed inversely correlated patterns such as between Form-A and *p*-Tolu-A (−0.65); Acet-A and *p*-Tolu-A (−0.70); Acetone and *p*-Tolu-A (−0.69), Croton-A (−0.50); Propion-A

and *p*-Tolu-A (−0.74); and Butyr-A and *p*-Tolu-A (−0.55). The majority of the carbonyls in the present study exhibited excellent correlations with ambient Form-A. The presence of strong positive correlations between the Form-A and the majority of other carbonyls, as observed in the present study, has been reported previously [1,30,33,38]. However, our results differ from previous reports with respect to the correlation patterns between Acet-A and a good number of the other carbonyls [13,14,33,38]. Strong positive correlations between Form-A and other carbonyls in this study, as observed for the 14 matching cases, implies that these carbonyls possibly resulted from the same or similar sources in this large industrial area. However, due to the variety of sources and sinks, ambient carbonyl concentration levels are affected by various factors [30]. Differences in reaction rate and life time (due to OH, NO<sub>3</sub>, O<sub>3</sub> and photolysis of each carbonyl as reported by Atkinson [24]) as well as different vertical mixing of carbonyls in different meteorological conditions (Ho et al. [38]) might affect the large variations in the correlations patterns.

In this section, we extended further to evaluate the correlations between the concentrations of carbonyls and other relevant odorous chemicals (e.g., reduced sulfur compounds (RSCs), VOCs (excluding carbonyls) and ammonia) measured concurrently during the same study period (Table 8B). (Discussions on other odorous compounds in the same study area will be dealt in our subsequent publications.) The results of correlation

Table 8  
Results of correlation analysis between carbonyls and other odorous pollutants

	Form-A	Acet-A	Acetone	Propion-A	Croton-A	Butyr-A	Benz-A	Isovaler-A	Valer-A	<i>p</i> -Tolu-A
(A) Correlation between different carbonyls										
Acet-A	0.20									
Acetone	<u>0.60</u>	−0.04								
Propion-A	0.16	0.33	0.01							
Croton-A	−0.08	0.31	<u>−0.50</u>	<u>0.41</u>						
Butyr-A	<u>0.44</u>	0.10	0.28	0.06	−0.07					
Benz-A	<u>0.48</u>	−0.17	0.34	−0.06	0.08	0.27				
Isovaler-A	<u>0.74</u>	<u>0.65</u>	<u>0.65</u>	<u>0.72</u>	<u>1.00</u>	<u>0.78</u>	−0.04			
Vale-A	0.15	−0.11	−0.03	−0.31	<u>0.88</u>	−0.06	<u>0.79</u>	<u>0.83</u>		
<i>p</i> -Tolu-A	<u>−0.65</u>	<u>−0.70</u>	<u>−0.69</u>	<u>−0.74</u>		<u>−0.55</u>	0.19	<u>0.47</u>	0.14	
(B) Correlation of carbonyls with the other concurrently determined odorous pollutants										
H <sub>2</sub> S	0.05	−0.30	0.01	−0.13	−0.09	−0.14	0.02	−0.25	0.15	−0.21
CH <sub>3</sub> SH	0.18	−0.05	0.09	−0.02	−0.24	0.21	0.11	−0.19	<u>0.57</u>	0.00
DMS	0.22	0.02	0.30	0.04	0.33	<u>0.39</u>	0.06	<u>−0.83</u>	<u>−0.67</u>	<u>0.92</u>
CS <sub>2</sub>	−0.26	−0.20	−0.14	−0.11	0.21	−0.34	−0.15	<u>−0.26</u>	<u>0.49</u>	0.15
DMDS	0.22	−0.06	0.10	−0.06	−0.12	0.28	0.09	<u>−0.71</u>	<u>−0.89</u>	
TVOC	−0.17	0.02	−0.10	−0.07	−0.12	0.04	−0.14	0.31	<u>0.38</u>	−0.21
B	<u>0.44</u>	<u>−0.39</u>	<u>0.38</u>	−0.07	<u>0.67</u>	0.31	0.34	<u>−0.75</u>	0.09	<u>0.60</u>
T	0.20	−0.09	0.20	−0.17	−0.12	<u>0.51</u>	0.21	0.02	0.23	−0.19
E	0.01	0.06	0.05	−0.09	−0.09	<u>0.36</u>	−0.05	−0.11	0.33	−0.24
MPX	0.03	0.01	0.03	−0.11	−0.07	<u>0.59</u>	−0.05	−0.23	0.33	−0.23
STY	0.03	0.03	−0.05	−0.08	<u>0.37</u>	<u>0.68</u>	−0.04	0.26	0.01	−0.21
OX	−0.01	0.10	0.07	−0.02	<u>0.79</u>	−0.06	0.01	0.08	0.38	−0.22
BB	−0.10	0.20	0.18	0.14		0.31	−0.34			
1,3,5-TMB	−0.11	<u>0.36</u>	−0.02	0.00	<u>0.67</u>	−0.07	−0.09	<u>1.00</u>	0.12	
1,2,4-TMB	−0.06	0.12	0.03	0.00	−0.01	−0.06	−0.06	<u>−0.69</u>	0.24	0.35
<i>p</i> -IPT	−0.14	0.01	−0.22	−0.10	<u>0.68</u>	−0.09	−0.04		−0.06	
<i>n</i> -BB	−0.35	<u>0.55</u>	−0.01	0.04		0.12	0.30			
NH <sub>3</sub>	<u>0.62</u>	<u>−0.38</u>	<u>0.47</u>	0.06	<u>1.00</u>	0.35	<u>0.56</u>	−0.16	−0.13	−0.30

Statistically significant values at  $P < 0.01$  level of significance have been underlined.

Table 9  
Conversion of carbonyl concentration into malodor degree<sup>a</sup>

Carbonyl compound	Reference																
	Present study								Ambient air in industrial site			Background urban air					
	All data	Industrial site	Non-industrial site	Daytime	Nighttime	Summer	Fall	Winter	[17]	[14]	[5]	[21]	[4]	[9]	[8]	[7]	[16]
Acet-A	2.1	2.1	2.1	2.2	2.1	2.1	2.3	2.0	1.2	1.4	1.6	0.8	1.5	1.6	2.0	1.9	0.9
Propion-A	2.1	2.1	2.2	2.4	2.0	2.2	2.1	1.7	0.8	0.6	0.7		0.6	0.5	1.4		0.1
Butyr-A	2.6	2.6	2.5	2.5	2.6	2.7	2.2	1.9	1.0	0.9	1.0			0.6	1.9		
Isovaler-A	1.9	1.8	2.0	2.1	1.2	1.9		1.5		0.5	1.1			0.4			
Valer-A	1.1	1.1	1.1	1.0	1.2	1.0		1.3		0.9	0.3						

Five offensive odorous pollutant data were used for comparison between the present and previous studies.

<sup>a</sup> First order equation for the calculation of malodor degree: Acet-A ( $Y = 1.01 \log X + 3.85$ ), Propion-A ( $Y = 1.01 \log X + 3.88$ ), Butyr-A ( $Y = 1.03 \log X + 4.51$ ), Isovaler-A ( $Y = 1.35 \log X + 6.01$ ) and Valer-A ( $Y = 1.36 \log X + 5.28$ ). To derive malodor degree ( $Y$ ),  $X$  terms are inserted as ppm concentration of odors.

analysis between the concentrations of 10 carbonyls (e.g., Form-A, Acet-A, Acetone, Propion-A, Croton-A, Butyr-A, Benz-A, Isovaler-A, Valer-A and *p*-Tolu-A) showed that significant correlations exist between 31 out of 158. However, out of those 31 significant cases, a total of 23 cases showed strong positive correlations.

### 3.6. Consideration of odor strength for ambient carbonyls

Because carbonyls belong to one of the major odorous components, assessment of their relative strength as odor constituents may be a valuable asset to discover their potential as odorous chemicals. From this respect, it is very desirable to explain the relationship between the concentrations of carbonyls and their efficacy as malodor. The raw concentration data of carbonyls can in fact be converted into the corresponding malodor degree (MD) by the empirical functions developed based on the threshold limit from air dilution sensory test (e.g., refs. [39–41]). Hence, as seen in Table 9, their concentrations are all converted and allocated into each respective sensory level of varying malodor strengths between 0 and 5. The results of the present study expressed in MD values have also been compared with their counterparts obtained from previous studies made in the other parts of world.

The odor intensity derived from the five carbonyls, assigned as the offensive odor component in Korea, is generally found to be significantly higher than those of other sites representing other environment types. The relative contribution of carbonyls measured in the present study towards the scale of malodor formation, as has been judged by the MD values, is generally found in the following descending order: Butyr-A > Acet-A  $\approx$  Propion-A > Isovaler-A > Valer-A. However, in all of the previous reports made either from the ambient air at industrial sites or in urban background air, maximum odor intensity was observed for the Acet-A followed by Butyr-A and Propion-A. Thus, the relative pattern observed in the present study fairly contrasts with those observed from most previous reports. According to the results of the present study focusing on the carbonyl distributions, Acet-A, Propion-A, Butyr-A and

Isovaler-A are the most dominant components of carbonyls in the ambient air of this large industrial area, which may exert certain influences on odor occurrences in the study area.

## 4. Conclusion

In the present study, the ambient concentrations and occurrence patterns of 12 individual carbonyls have been investigated as the key constituent of odorous pollutants in the multiple locations surrounding the Ban wall industrial area (August 2004 to September 2005). The carbonyl dataset obtained in a series of field experiments has been evaluated and compared in terms of the mean concentrations, concentration ratios, and relative composition (%). Moreover, the results were also converted into the odor intensity towards malodor formation. Most of the carbonyls were present in sizeable amounts in most of the samples collected from diverse site characteristics throughout the study. However, Acrolein and *m*-Tolu-A were present in only limited cases, while *o*-Tolu-A was not detected in any of the samples. The results in the present study have been compared with the previously available reports made from other parts of the world. The magnitudes of carbonyl data in the present study are generally found to be substantially higher than most other studies. The Acet-A and Form-A were observed to be the most dominant components in the ambient air of this large industrial area throughout the study period.

The ambient concentrations, when examined for the spatial variation patterns between industrial and non-industrial site types, were found to be statistically insignificant and thus of negligible importance. However, the seasonal and diurnal variations in ambient concentrations of carbonyls were found to be fairly significant. The findings of higher carbonyl levels during daytime and summer in most cases suggest the potentially important roles of meteorological conditions and the related chemical conditions. The results of the correlation study indicated miscellaneous sources for most of the carbonyls as well as the other relevant odorous pollutants, with a few exceptions. In the present study the substantially

higher relative composition (%) and malodor degree of the five offensive pollutants were found along with the lower ratio values of carbonyl concentrations ( $C_1/C_2$  and  $C_2/C_3$ ). Based on the observations of the highest absolute mean concentration of Acet-A ( $\approx$ Propion) in concert with the lowest  $C_1/C_2$  and  $C_2/C_3$  ratio values, the distribution of carbonyls is suspected to be affected by the potential use of ethanol containing fuels or chemicals in this area. Furthermore, the comparatively high proportion of the five major malodor carbonyls and the associated strong odor intensity in the present study suggests moderately disquieting circumstances in this industrial area.

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