



## Volatile organic compounds at an urban monitoring station in Korea

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### ABSTRACT

Measurements of 56 volatile organic compounds (VOC) were undertaken at a monitoring site in Seoul, Korea in 2004. The VOC pollution at the site was evaluated for both functional groups and individual compounds. The highest concentrations for the functional groups were recorded by aromatic (AR: 430 ppbC) followed by paraffin (PR), olefin (OF), and alkyne (AK). The mean concentrations of individual VOCs ranged from 0.05 ppb (1-hexene) to 39.8 ppb (toluene). For the VOC groups, there were peak concentrations during winter (AK and OF) and summer (AR). Although most aromatic VOCs generally peaked during summer, this was not true for benzene (e.g., winter peak). The distribution of VOCs at the study site was characterized by significantly enhanced concentrations of toluene and aromatic VOCs from local industrial and mobile sources. Despite excursions that were occasionally observed from aromatic groups or benzene, strong correlations occurred frequently between different groups and between individual components. The overall results of this study suggest that anthropogenic emissions have contributed greatly to increases in VOC pollution at the study site.

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### 1. Introduction

Volatile organic compounds (VOCs) are gaseous non-methane organic compounds (NMOCs) with carbon atoms of C<sub>2</sub> to C<sub>12</sub>. In general, they are produced and emitted by natural and anthropogenic activities. Man-made VOC emissions typically come from either mobile sources (e.g., vehicular emissions) or stationary sources (industrial emissions). Emissions of aromatic hydrocarbons, although constituting a fairly large proportion of NMOC, come from gasoline and diesel-engine vehicles [1–3]. As such, vehicular exhaust is invariably one of the major contributors (more than 50%) of NMOC in urban/suburban areas. Gasoline exhaust is four times larger than diesel exhaust according to Watson et al. [4]. Alkynes are the major products of internal combustion engines, while C<sub>5</sub>–C<sub>8</sub> saturated NMOCs usually come from unburned vehicular emissions [5]. Hence, VOC emissions from petroleum-related industries pose an imminent threat to the environment and human health. Many studies suggest that hazardous air pollutant emissions directly impact human health in urban areas [6,7]. The concentration levels of VOCs at some US sites were high enough to cause cancer, birth defects, and other serious illnesses [8,9].

VOCs can cause a large amount of pollution on both a local and regional scale as they are some of the most significant atmospheric pollutants emitted from anthropogenic sources (e.g., acid rain or

photochemical ozone production) [10]. For stationary sources such as coal combustion, the magnitude of VOC emissions grows with the expansion of domestic consumption. China's economic growth has made it the world's largest coal consuming country. The amount of coal consumed in China was 2062 million tons in 2004 which was equivalent to about 34% of the global consumption [11].

In Korea, Seoul is the largest city with a population of over 10 million. There are 2.78 million registered vehicles in the city according to the annual report of the Korean Ministry of Construction and Transportation [12]. Hence, as expected, photochemical processes strongly influence the ambient air quality in Seoul [13]. In this study, VOC measurement data gathered in Seoul were analyzed to find the fundamental characteristics of VOC distribution in an urban area. The level of VOC pollution at the study site was monitored routinely at one of the Photochemical Assessment Monitoring Stations (PAMS). In this paper, PAMS data for 56 individual VOCs were analyzed in several ways.

### 2. Materials and methods

The study site represents PAMS III type. The PAMS type III is commonly designated at the downwind position where maximum ozone concentration occurs [14]. The city of Seoul currently operates and manages a PAMS system. Its operation in the Sung-Su (SS) district began in November of 2001 and ceased in November 2005 because officials merged the station with a nearby facility (Fig. 1). The VOC data used for this study were collected over 1-year period in 2004 (January through December). The study area is near the

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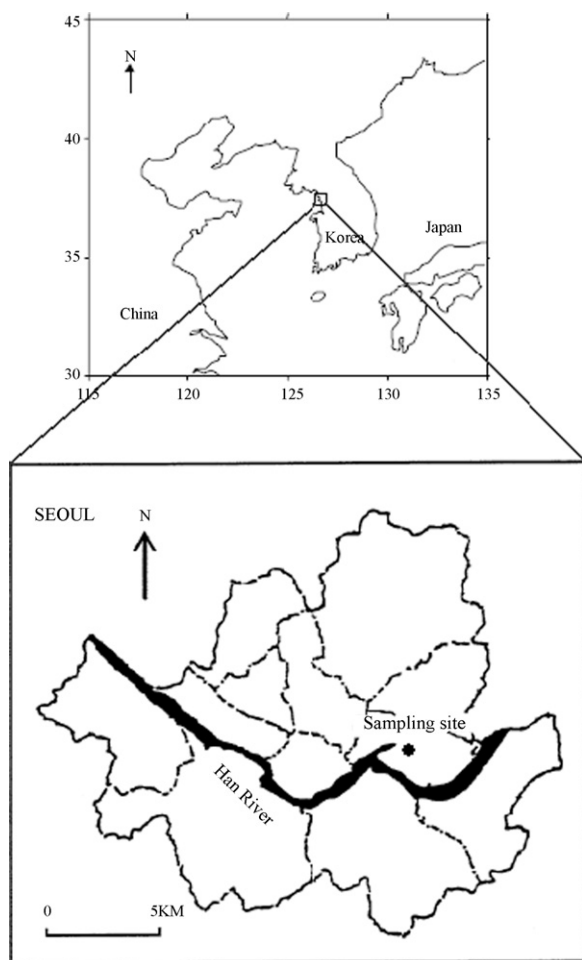


Fig. 1. A geographical map of the study site. Sung-Su station is located in the eastern part of Seoul in Korea.

central part of Seoul where there are various municipal facilities, small manufacturing units, and a large number of apartment complexes. The monitoring station was placed on the top of a 3-story building, a few hundred meters from a busy road. The air quality at the site was affected by traffic-related sources and industrial activities in the area. The station was meant to detect high ozone events and to describe precursor transportation patterns in the area.

To measure concentrations of individual hydrocarbons, a combination of the on-line thermal desorption system (Unity/Air Server, Markes) and the GC/Deans switch/Dual FID system (Varian 3800 GC, USA) was employed. As part of the quality assurance (QA) procedures, calibration mixtures and blanks were introduced to the thermal desorbing system in the same way as ambient air samples. The calibration mixtures were prepared as secondary standards. They were diluted from a primary standard supplied by Air Liquide America Specialty Gases LLC (Plumsteadville, PA, US) and stored in a pressurized canister. Primary standards made of multi-component mixtures were prepared in ultrapure nitrogen gas to certified concentrations. Hourly measurements of the air quality were made at the site and all the data were collected, stored, and transmitted to the Seoul Metropolitan Institute of Public Health and Environment via the Internet.

Acquisition of PAMS data in a continuous, on-line mode can offer a unique opportunity to describe the behavior of VOCs in relation to various environmental conditions. The quality of the VOC data acquired as a result of the PAMS operation was tested routinely as

part of a QA task. These processes covered peak splitting, elevated blank levels, merging with neighboring peaks, and the merging of peaks with unknown and unreported organic compounds (e.g., Derwent et al. [15]). The QA program for the VOC measurements in this study was established by referring to the US EPA/600-R-98/161, technical assistance document for sampling and analysis of ozone precursors.

### 3. Results and discussion

#### 3.1. The overall patterns of VOC distribution

Because the station is located near a busy thoroughfare and is surrounded by buildings and small manufacturing facilities, the observed VOC distributions may reflect the mixed effects of diverse anthropogenic source components such as: motor vehicle exhaust, gasoline evaporation, paint solvents, liquefied petroleum gas (LPG), and natural gas. Table 1 provides information on individual VOCs including their chemical formulas. The table classifies the VOCs into four major groups: alkyne (AK), aromatic (AR), olefin (OF), and paraffin (PR). (Note that the AK group consists of a single compound, acetylene.) Moreover, a statistical summary of the mean VOC concentrations measured at hourly intervals during the entire study period is also shown for each individual component in Table 1. The results indicate that the concentration levels of most individual VOCs are generally low with hourly mean values predominantly below 1 ppb (for 32 out of the 56 individual VOCs). The lowest value of  $0.05 \pm 0.28$  ppb (median = 0.03,  $N = 8003$ ) was measured for 1-hexene, whereas the highest mean value of  $39.8 \pm 23.0$  ppb (median = 35.1,  $N = 8641$ ) for toluene. High concentration levels of toluene have been reported in urban areas in the past [15].

To aid the interpretation of the VOC data sets measured from the SS station, a detailed analysis was undertaken to compare concentration levels between major groups (such as AK, AR, OF, and PR) and between some important individual species (mainly BTEX species: benzene, toluene, ethylbenzene, *m/p*-xylene, and *o*-xylene) (Table 2). For this comparison, the concentration of each individual VOC component is given in ppb (parts per billion by volume of compound), as shown in Table 1. All major VOC groups are expressed in ppbC (parts per billion by volume as carbon) units, as this concept is more logical to assess the quantity of mixed hydrocarbon constituents. If all VOC groups are compared in terms of the magnitude of concentration (ppbC unit), the highest mean values were seen for the AR group (430 ppbC), followed by PR group (250 ppbC). On the other hand, the lowest mean values were recorded for the AK group (5.68 ppbC). The negative influence of AR on human health is well-known, as AR contributes to the formation of photochemical smog [16]. The AR group is generally emitted from fossil fuel combustion [2,17]. Its proportion in fossil fuels (41–52%) is larger than all other functional groups (e.g., PR group (28–47%) or the OF group (7–12%) [18]).

To learn more about the distribution of VOCs in the study area, their frequency patterns were examined as shown in Fig. 2. This comparison was also made for both the VOC groups and individual BTEX species. The results indicate that the distribution of many VOCs is not in normal shape because very high concentrations can occur at certain hours due to strong emission activities (e.g., acetylene emission during traffic hours). There are also large differences in concentration levels between the VOCs groups and between individual species. The peak concentrations for the AR group were generally observed at 400 ppbC ( $N = 1724$ ), while those of the PR, OF, and AK groups were seen at 200, 30, and 6 ppbC, respectively. In Fig. 2B, the results for the BTEX species are also compared. The occurrence of their peak concentration values were observed as follows: toluene (30 ppb), ethylbenzene (4 ppb), and *m/p*-xylene

**Table 1**  
Basic information for the 56 VOCs measured at the Sung-Su station of Seoul, Korea in 2004 with a statistical summary (all concentrations in ppb)

VOC No.	Full name	Grouping <sup>a</sup>	Chemical structure	Mean	Median	S.D.	Minimum <sup>b</sup>	Maximum	N <sup>c</sup>	N (at DL) <sup>d</sup>
1	Ethane	PR	CH <sub>3</sub> CH <sub>3</sub>	3.85	3.10	3.07	0.05	49.7	8635	24
2	Ethylene	OF	CH <sub>2</sub> =CH <sub>2</sub>	1.73	1.30	1.53	0.05	14.3	8638	21
3	Propane	PR	CH <sub>3</sub> CH <sub>2</sub> CH <sub>3</sub>	9.57	8.13	6.45	0.03	302	8652	7
4	Propylene	OF	CH <sub>3</sub> CH=CH <sub>2</sub>	2.12	1.97	0.81	0.01	18.7	8603	56
5	Isobutane	PR	CH(CH <sub>3</sub> ) <sub>2</sub> CH <sub>3</sub>	3.16	2.50	5.15	0.05	241	8631	27
6	<i>n</i> -Butane	PR	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	5.37	4.40	5.32	0.03	233	8634	19
7	Acetylene	AK	C <sub>2</sub> H <sub>2</sub>	2.84	2.30	1.89	0.01	16.8	8600	58
8	<i>trans</i> -2-Butene	OF	CH <sub>3</sub> CH=CHCH <sub>3</sub>	0.36	0.30	0.75	0.003	43.0	8633	26
9	1-Butene	OF	CH <sub>2</sub> =CHCH <sub>2</sub> CH <sub>3</sub>	0.22	0.18	0.37	0.00	11.9	8640	18
10	<i>cis</i> -2-Butene	OF	CH <sub>3</sub> CH=CHCH <sub>3</sub>	0.22	0.15	0.89	0.01	67.1	8643	14
11	Cyclopentane	PR	C <sub>5</sub> H <sub>10</sub>	1.22	0.90	1.94	0.00	152	8616	39
12	Isopentane	PR	C <sub>2</sub> H <sub>5</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	2.24	1.88	2.81	0.01	164	8616	42
13	<i>n</i> -Pentane	PR	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	1.20	1.02	0.89	0.00	34.4	8645	13
14	<i>trans</i> -2-Pentene	OF	C <sub>2</sub> H <sub>5</sub> CH=CHCH <sub>3</sub>	0.19	0.14	0.47	0.02	23.5	8630	29
15	1-Pentene	OF	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH=CH <sub>2</sub>	0.11	0.10	0.31	0.01	14.2	8619	40
16	<i>cis</i> -2-Pentene	OF	C <sub>2</sub> H <sub>5</sub> CH=CHCH <sub>3</sub>	0.10	0.08	0.40	0.004	15.2	8320	339
17	2,2-Dimethylbutane	PR	CH <sub>3</sub> CH <sub>2</sub> C(CH <sub>3</sub> ) <sub>2</sub> CH <sub>3</sub>	0.30	0.22	0.66	0.02	45.8	8633	26
18	2,3-Dimethylbutane	PR	(CH <sub>3</sub> ) <sub>2</sub> CHCH(CH <sub>3</sub> ) <sub>2</sub>	0.28	0.25	0.37	0.02	12.9	8625	34
19	2-Methylpentane	PR	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	0.14	0.10	0.36	0.01	11.9	8564	50
20	3-Methylpentane	PR	C <sub>2</sub> H <sub>5</sub> CH(CH <sub>3</sub> )C <sub>2</sub> H <sub>5</sub>	0.13	0.10	0.36	0.01	12.1	8598	45
21	Isoprene	OF	CH <sub>2</sub> =CHC(CH <sub>3</sub> )=CH <sub>2</sub>	0.34	0.14	0.66	0.02	10.1	8620	39
22	1-Hexene	OF	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH=CH <sub>2</sub>	0.05	0.03	0.28	0.00	10.5	8004	654
23	<i>n</i> -Hexane	PR	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH <sub>3</sub>	3.30	2.37	2.77	0.02	22.2	8650	8
24	Methylcyclopentane	PR	C <sub>5</sub> H <sub>9</sub> CH <sub>3</sub>	4.38	3.04	4.01	0.02	40.0	8646	9
25	2,4-Dimethylpentane	PR	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	6.98	0.03	28.6	0.01	118	17	8642
26	Benzene	AR	C <sub>6</sub> H <sub>6</sub>	0.84	0.72	1.83	0.10	164	8655	4
27	Cyclohexane	PR	C <sub>6</sub> H <sub>12</sub>	1.57	1.18	1.31	0.02	14.1	8656	2
28	2-Methylhexane	PR	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	0.43	0.37	0.47	0.01	13.7	8645	13
29	2,3-Dimethylpentane	PR	C <sub>2</sub> H <sub>5</sub> CH(CH <sub>3</sub> )CH(CH <sub>3</sub> ) <sub>2</sub>	0.16	0.11	0.47	0.01	14.0	7042	1615
30	3-Methylhexane	PR	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>3</sub>	0.44	0.37	0.47	0.01	13.5	8644	13
31	2,2,4-Trimethylpentane	PR	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub> C(CH <sub>3</sub> ) <sub>3</sub>	0.45	0.36	0.44	0.01	11.4	8627	28
32	<i>n</i> -Heptane	PR	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CH <sub>3</sub>	0.60	0.51	0.52	0.01	13.4	8650	7
33	Methylcyclohexane	PR	C <sub>6</sub> H <sub>11</sub> CH <sub>3</sub>	0.54	0.46	0.54	0.01	14.3	8648	10
34	2,3,4-Trimethylpentane	PR	(CH <sub>3</sub> ) <sub>2</sub> CHCH(CH <sub>3</sub> )CH(CH <sub>3</sub> ) <sub>2</sub>	0.15	0.04	1.45	0.01	40.4	2610	6046
35	Toluene	AR	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	39.8	35.1	23.0	0.06	143	8641	3
36	2-Methylheptane	PR	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	1.71	1.47	1.17	0.03	11.5	8609	91
37	3-Methylheptane	PR	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>3</sub>	1.20	1.00	0.85	0.02	12.1	8614	56
38	<i>n</i> -Octane	PR	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> CH <sub>3</sub>	0.31	0.26	0.39	0.01	11.8	8649	6
39	Ethylbenzene	AR	C <sub>6</sub> H <sub>5</sub> C <sub>2</sub> H <sub>5</sub>	4.35	3.38	3.31	0.03	30.3	8650	5
40	<i>m/p</i> -Xylene	AR	C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub>	5.25	4.68	3.24	0.08	60.8	8650	5
41	Styrene	AR	C <sub>6</sub> H <sub>5</sub> CH=CH <sub>2</sub>	0.51	0.48	0.34	0.04	8.12	8652	6
42	<i>o</i> -Xylene	AR	C <sub>6</sub> H <sub>4</sub> (CH <sub>3</sub> ) <sub>2</sub>	2.08	1.84	1.25	0.01	20.8	8649	7
43	<i>n</i> -Nonane	PR	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> CH <sub>3</sub>	1.52	1.13	1.42	0.04	16.9	8644	12
44	Isopropylbenzene	AR	C <sub>6</sub> H <sub>5</sub> CH(CH <sub>3</sub> ) <sub>2</sub>	0.68	0.50	1.08	0.001	84.4	8616	11
45	<i>n</i> -Propylbenzene	AR	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	0.25	0.21	0.34	0.02	11.4	8648	7
46	<i>m</i> -Ethyltoluene	AR	C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	0.65	0.57	0.44	0.12	11.7	8643	14
47	<i>p</i> -Ethyltoluene	AR	C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	0.37	0.31	0.31	0.01	9.33	8652	6
48	1,3,5-Trimethylbenzene	AR	C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>3</sub>	0.90	0.77	0.53	0.07	11.3	8649	7
49	<i>o</i> -Ethyltoluene	AR	C <sub>2</sub> H <sub>5</sub> C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	0.32	0.28	0.37	0.02	12.1	8649	6
50	1,2,4-Trimethylbenzene	AR	C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>3</sub>	1.07	0.99	0.53	0.03	11.6	8649	6
51	<i>n</i> -Decane	PR	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>8</sub> CH <sub>3</sub>	2.31	2.01	1.36	0.02	15.1	8649	6
52	1,2,3-Trimethylbenzene	AR	C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>3</sub>	0.69	0.56	0.53	0.02	12.0	8648	6
53	<i>m</i> -Diethylbenzene	AR	C <sub>6</sub> H <sub>4</sub> (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	0.24	0.23	0.27	0.01	11.7	8653	5
54	<i>p</i> -Diethylbenzene	AR	C <sub>6</sub> H <sub>4</sub> (C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	0.30	0.27	0.28	0.02	9.85	8653	5
55	<i>n</i> -Undecane	PR	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>9</sub> CH <sub>3</sub>	1.10	0.93	0.57	0.01	14.6	8650	5
56	<i>n</i> -Dodecane	PR	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>10</sub> CH <sub>3</sub>	0.61	0.52	0.46	0.01	20.8	8648	8

<sup>a</sup> AK: Alkyne; AR: Aromatic; OF: Olefin; and PR: Paraffin.

<sup>b</sup> Minimum values above detection limit (DL).

<sup>c</sup> N: number of all hourly measurement data above detection limit (DL) values.

<sup>d</sup> N (at DL): number of hourly data at below DL (BDL) values.

(4 ppb). In contrast, the maximum frequency for benzene was a much smaller value (1 ppb). The relative dominance of the AR group and toluene component may be caused by the effects of traffic and industrial activities as well as solvent use (e.g., small manufacturing facilities within the apartment factory complexes in the area) [18–20]. A recent study of Geng et al. [21] reported that the aromatic was the main contributor to O<sub>3</sub> chemical production in Shanghai to account for approximately 79% of the O<sub>3</sub> in the study area.

To facilitate the interpretation of VOC behavior in the area impacted by strong man-made activities, a daily variation pattern

of basic meteorological parameters (e.g., ultraviolet (UV), wind speed (WS), wind direction (WD) and temperature (TEMP)) were also investigated, as shown in Fig. 3. The results indicated that the strongest oscillation intensity of UV was found from 120 to 220 Julian days (JD), and such intensity significantly declined at both the intervals for 1–20 JD and from 310 to 366 JD. UV intensity was reflected on the changes in the temperature levels. The temperature distribution steadily increased from the beginning of the study, reaching its highest value at 225 JD. When the daily variation pattern of wind speed was examined, the results indicated that

**Table 2**  
A statistical summary of major VOCs groups and individual BTEX components

Group <sup>a</sup>	Mean	Medium	S.D.	Minimum	Maximum	N
<b>[A] VOCs groups (ppbC)</b>						
AK	5.68	4.60	3.78	0.02	33.5	8600
AR	430	392	217	5.70	1609	8658
OF	17.0	14.2	15.4	0.20	372	8659
PR	250	227	134	1.90	2067	8658
Component <sup>b</sup>	Mean	Medium	S.D.	Minimum	Maximum	N
<b>[B] Individual BTEX components (ppb)</b>						
B	0.82	0.72	0.51	0.10	16.4	8655
T	39.8	35.1	23.0	0.06	143	8641
EB	4.35	3.38	3.31	0.04	30.3	8650
<i>m/p</i> -X	5.25	4.68	3.24	0.08	60.8	8650
<i>o</i> -X	2.08	1.84	1.24	0.03	20.8	8649

<sup>a</sup> Acronyms for VOCs groups: AK (alkyne), AR (aromatic), OF (olefin), and PR (paraffin).

<sup>b</sup> Acronyms for individual BTEX components: B (benzene), T (toluene), EB (ethylbenzene), *m/p*-X (*m/p*-xylene), and *o*-X (*o*-xylene).

relatively strong winds prevailed both at the beginning (from 1 to 90) and near the end of the study period (from 317 to 360).

### 3.2. Seasonal variation patterns of VOC

To examine the temporal variation patterns of VOCs, the daily mean values of the major VOC groups and five BTEX components were plotted in Fig. 4. Values as high as several hundred ppbC were in the AR group, while the lowest values at around 10 ppbC were usually in the AK group. In the case of BTEX, the concentration levels of benzene were maintained at quite low values around 1 ppb. According to this comparison, the values of most BTEX components increased from 120 to 180 or 120 to 220 Julian days. In addition, there were significantly large variations in the concentration of toluene with the frequent occurrence of exceptionally large values (up to several tens of ppb) during the summer. However, slightly reduced levels of benzene (i.e., less than 0.8 ppb) were noted most commonly during the Julian days 191 to day 285.

As a means of assessing the temporal distribution of VOCs at the study site, seasonal patterns were examined for both VOC groups and individual BTEX species. The results shown in Fig. 5 indicate that the AK and OF groups showed maximum values during winter with mean values of 7.72 and 18.6 ppbC, respectively. Although there is no direct reference to explain the relative enhancement of AK levels during the winter, there were some efforts to assess the seasonal patterns of acetylene in terms of its concentration ratio with total hydrocarbon (A/THC ratio) [13]. In light of the fact that traffic emission is a major source of acetylene, Na and Kim [13] explained the relatively high A/THC ratio during winter as the result of a decrease in non-traffic source activities (e.g., gasoline evaporation and the use of solvents). The cause of such differences in temporal variation patterns was also studied in a Taiwanese urban area [22]. Due to a strong seasonality, temperature inversion is suspected to promote a maximum concentration of pollutants in the winter, while such an effect is not significant enough during the summer. In contrast to the general expectation, the AR group exhibited the highest value during the summer (527 ppbC) and the lowest value in winter (328 ppbC). In the case of the PR group, the pattern was slightly different from the other groups with its values ranging from 225 in the fall to 297 ppbC in the spring. One may speculate that temporal factors, because of the various environmental properties of VOCs, may interact with sources and sinks of VOC groups in a complicated manner [23].

If the temporal patterns of aromatic VOC components are compared between seasons (Fig. 5B), most of them (except benzene) reach their highest values in summer. This may partially be because sources of TEX (toluene, ethylbenzene, and xylene) are comparable

to each other when in the form of solvents or evaporated gas. Previous studies have shown that the seasonal patterns of aromatic VOCs are generally characterized by peaks in the summer due to their strong volatility [13].

### 3.3. Diurnal variation patterns of VOC

In Fig. 6, the diurnal variation patterns of VOCs were plotted using the hourly mean concentration data for both the VOC group and individual BTEX components. For the VOC groups, the concentrations for the AK, OF, and PR groups increased gradually so that the highest values occurred around midday. The absolute amplitude of diurnal variations (between maximum and minimum concentrations) also varied greatly between VOC groups: as 3.58 (AK), 11.3 (OF), and 130 ppbC (PR). In contrast, the night patterns were dominated (e.g., between 16:00 and 21:00) by the AR group with an amplitude of diurnal variability exceeding 177 ppbC (in the range between 335 and 512 ppbC). If the amplitude of diurnal variation is compared in terms of relative magnitude (or by percentage), it varied: OF (60%), AK (56%), PR (49%), and AR (41%). Similar to the relative patterns between functional groups, there were many differences detected in diurnal variations for individual BTEX components. The maximum concentration levels of benzene and *o*-xylene occurred at noon with the amplitude of variation at 1.00 and 2.25 ppb, respectively. In contrast, ethylbenzene recorded its highest values at night (4.06 and 4.59 ppb). In the case of toluene, the highest concentration levels (51.1 ppb) were mainly observed during the afternoon, while the lowest (28.5 ppb) were found in the morning. For *m/p*-xylene, its concentration ranged from 4.64 to 5.66 ppb, reaching its maximum value at noon. If the relative amplitude of diurnal variation is compared between the individual VOC components, it decreased: toluene (57%), benzene (29%), *m/p*-xylene (20%), ethylbenzene (20%), and *o*-xylene (17%).

The diurnal variations of these aromatic components are reported to be affected most by such factors as traffic density (e.g., rush hour in early morning and evening time) [24]. An increase in evaporative emissions can also be accelerated by elevated temperatures in the afternoon. Moreover, it should also be considered that many types of man-made activities (painting, coating, printing activities, dry cleaning, solvent usage, etc.) occur intensively during normal daily work hours (09:00–18:00). As such, all of these conditions can facilitate the emissions of VOCs in the afternoon rather than in the morning or at night. Therefore, evaporative emission is likely to be as important as vehicle-related emission [25,26].

The diurnal data sets were initially examined for all seasons to analyze the short-term variability of VOCs from a different perspective (Fig. 6). A comparison based on two comparable criteria (i.e.,

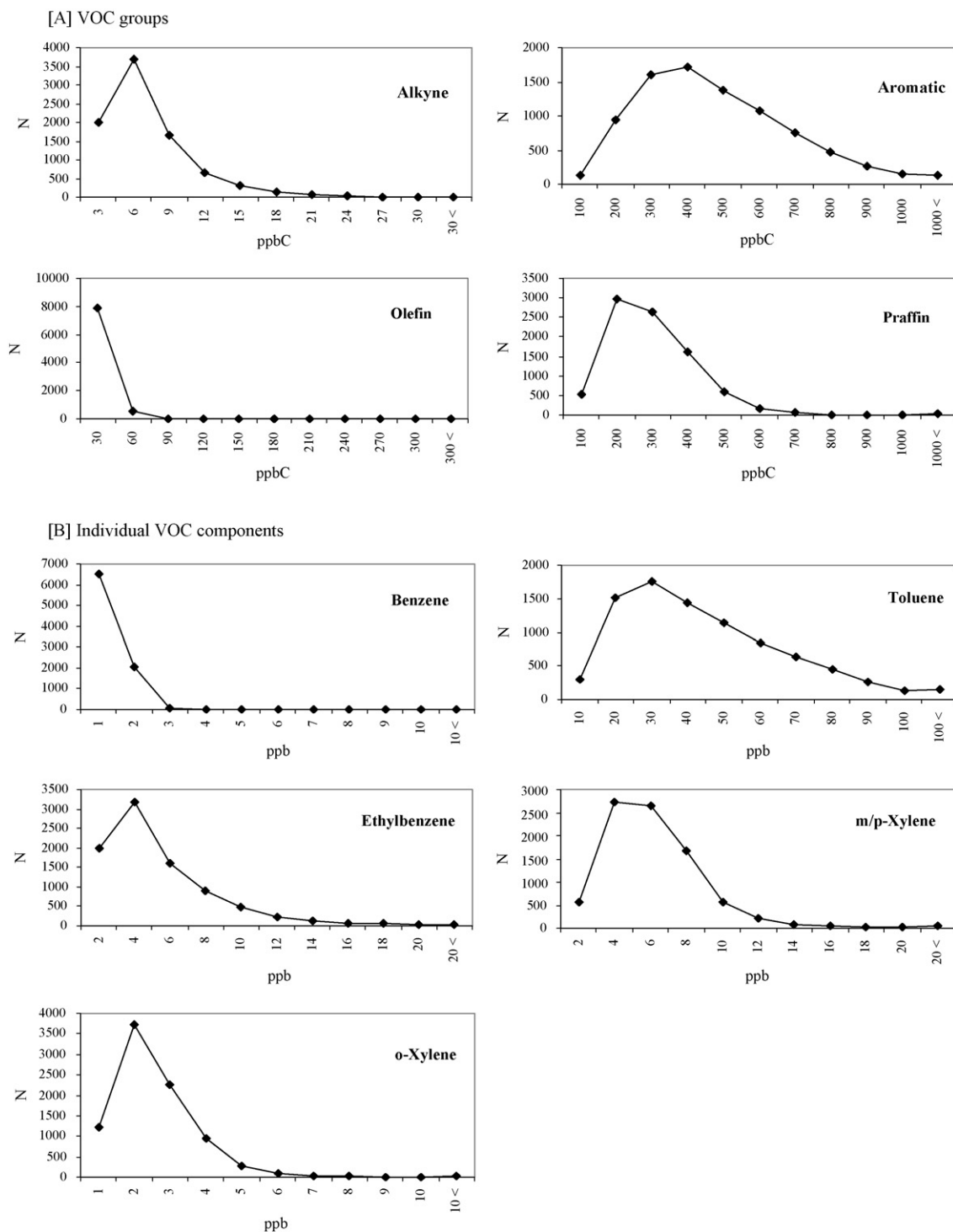


Fig. 2. The frequency distribution of VOC data measured at Sung-Su station in 2004 (by hourly data sets).

diurnal vs. seasonal) indicated that differences in relative patterns are significant between the AR group and the other groups. For the AR group, the maximum values were found most frequently in the late afternoon in all four seasons (i.e., between 16:00 and 21:00). Concentration levels rose for the AR group (over 400 ppb) during the spring and summer periods. The other groups (AK, OF, and PR groups) consistently exhibited the highest concentrations at noon for most seasons. Ethylene, acetylene and propylene are mainly emitted from vehicles [13,27]. In an estimate of tail pipe

emissions by petrol and diesel-powered engines, Guicherit [28] reported high concentration levels from individual components of such functional groups as AK, OF, and PR. Therefore, the peak values found at noon indirectly confirm that vehicular and evaporative emissions are stronger at midday.

The analysis of BTEX distributions showed that the highest recorded values occurred most frequently during summer, while amplitudes of diurnal variation declined for ethylbenzene, o-xylene, and m/p-xylene. However, in the summer pattern for ben-



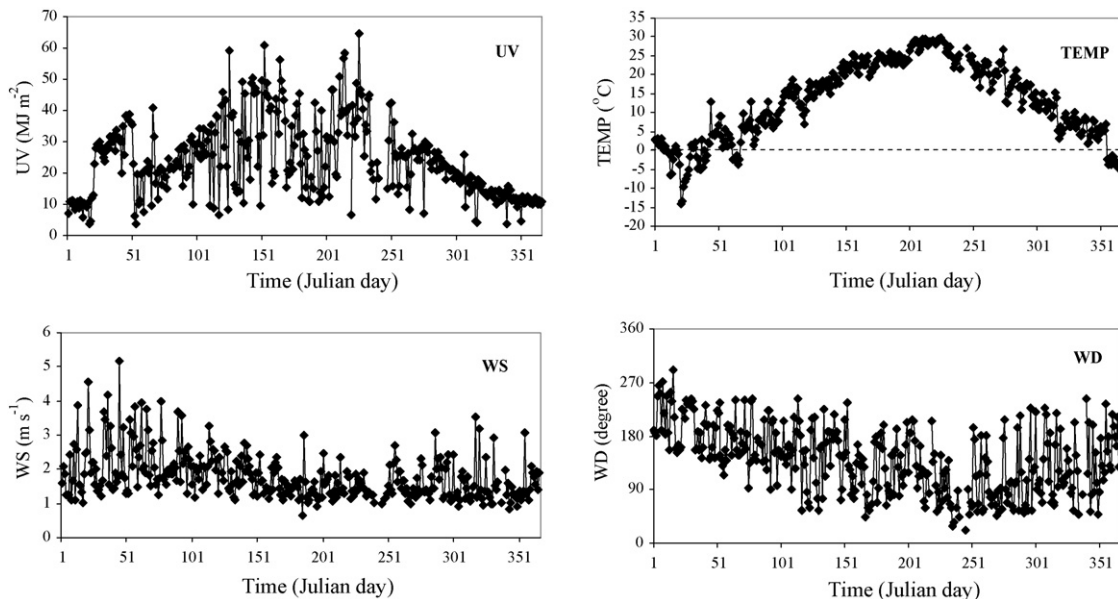


Fig. 3. Daily variation patterns of basic meteorological parameters measured at the SS site: ultraviolet (UV), temperature (TEMP), wind speed (WS), and wind direction (WD).

zene, it has a slight delay in its peak relative to the others (at 13:00). On the other hand, the pattern for *m/p*-xylene was complicated enough to show its maximum values either in the afternoon or at night. In the case of ethylbenzene, the diurnal variation patterns were consistent throughout the year, although unusual patterns

existed during the morning and night in the summer. The concentrations of toluene increased consistently at night (e.g., between 17:00 and 21:00) despite strong seasonal variability. Similar to this study, researchers observed enhanced concentration levels of toluene at night at three urban locations in Hong Kong [29].

**Table 3**  
The results of correlation analysis between the different VOC data sets

		AK	AR	OF	PR	B	T	EB	<i>m/p</i> -X	
[A] The relationship between VOC groups and individual VOC components (the number ( <i>N</i> ) of matching data is 366 in all cases)										
AR	<i>r</i> <sup>a</sup>	0.243 (II) <sup>b</sup>								
	<i>P</i> <sup>c</sup>	2.55E-06								
OF	<i>r</i>	0.59 (IV)	0.383 (III)							
	<i>P</i>	1.03E-35	3.09E-14							
PR	<i>r</i>	0.569 (IV)	0.785 (IV)	0.647 (IV)						
	<i>P</i>	8.45E-33	8.98E-78	8.22E-45						
B	<i>r</i>	0.775 (IV)	0.444 (III)	0.701 (IV)	0.715 (IV)					
	<i>P</i>	1.30E-74	4.06E-19	1.97E-55	1.38E-58					
T	<i>r</i>	0.263 (II)	0.959 (IV)	0.335 (III)	0.789 (IV)	0.419 (III)				
	<i>P</i>	3.31E-07	9.29E-202	4.75E-11	4.38E-79	5.38E-17				
EB	<i>r</i>	-0.041	0.704 (IV)	0.189 (I)	0.313 (II)	0.113	0.534 (IV)			
	<i>P</i>	4.34E-01	4.30E-56	2.77E-04	9.21E-10	3.07E-02	2.22E-28			
<i>m/p</i> -X	<i>r</i>	0.157 (I)	0.822 (IV)	0.305 (II)	0.541 (IV)	0.321 (II)	0.684 (IV)	0.882 (IV)		
	<i>P</i>	2.59E-03	4.02E-91	2.55E-09	3.19E-29	3.22E-10	7.70E-52	3.81E-121		
<i>o</i> -X	<i>r</i>	0.077	0.815 (IV)	0.321 (II)	0.505 (IV)	0.297 (II)	0.662 (IV)	0.92 (IV)	0.971 (IV)	
	<i>P</i>	1.41E-01	2.28E-88	3.22E-10	4.32E-25	6.87E-09	1.54E-47	2.28E-150	1.01E-228	
		AK	AR	OF	PR	B	T	EB	<i>m/p</i> -X	
[B] The relationship between meteorological parameters and the VOC groups as well as individual BTEX components (In all cases, the number ( <i>N</i> ) of matching data = 355–366) <sup>d</sup>										
UV	<i>r</i>	-0.34 (III)	0.22 (I)	-0.117	-0.006	-0.212 (I)	0.159 (I)	0.42 (III)	0.268 (II)	0.33 (II)
	<i>P</i>	3.87E-11	2.67E-05	2.69E-02	9.10E-01	5.27E-05	2.55E-03	9.79E-17	2.64E-07	1.53E-10
RH	<i>r</i>	0.066	0.165 (I)	0.202 (I)	0.086	0.114	0.176 (I)	0.116	0.169 (I)	0.142 (I)
	<i>P</i>	2.08E-01	1.54E-03	9.96E-05	1.00E-01	2.92E-02	7.19E-04	2.65E-02	1.17E-03	6.51E-03
WS	<i>r</i>	-0.316 (II)	-0.248 (II)	-0.385 (III)	-0.200 (I)	-0.201 (I)	-0.217 (I)	-0.266 (II)	-0.307 (II)	-0.267 (II)
	<i>P</i>	1.13E-09	2.24E-06	5.43E-14	1.49E-04	1.37E-04	3.73E-05	3.65E-07	3.47E-09	3.29E-07
TEMP	<i>r</i>	-0.417 (III)	0.44 (III)	0.012	0.041	-0.278 (II)	0.354 (III)	0.646 (IV)	0.547 (IV)	0.579 (IV)
	<i>P</i>	1.54E-16	1.96E-18	8.21E-01	4.39E-01	8.55E-08	4.86E-12	8.25E-44	2.04E-29	1.55E-33

Refer to Table 2 for information of all acronyms for VOC groups and components.

<sup>a</sup> Correlation coefficient.

<sup>b</sup> Roman letters given in the parenthesis denote: (1) no class (the weakest correlation strength range):  $P \geq 10^{-2}$ ; (2) class I:  $10^{-5} \leq P < 10^{-2}$ ; (3) class II:  $10^{-10} \leq P < 10^{-5}$ ; (4) class III:  $10^{-20} \leq P < 10^{-10}$ ; and (5) class IV:  $P < 10^{-20}$ .

<sup>c</sup> Probability of no correlations.

<sup>d</sup> The acronyms used for meteorological parameters: UV (ultraviolet), WS (wind speed), and TEMP (temperature).

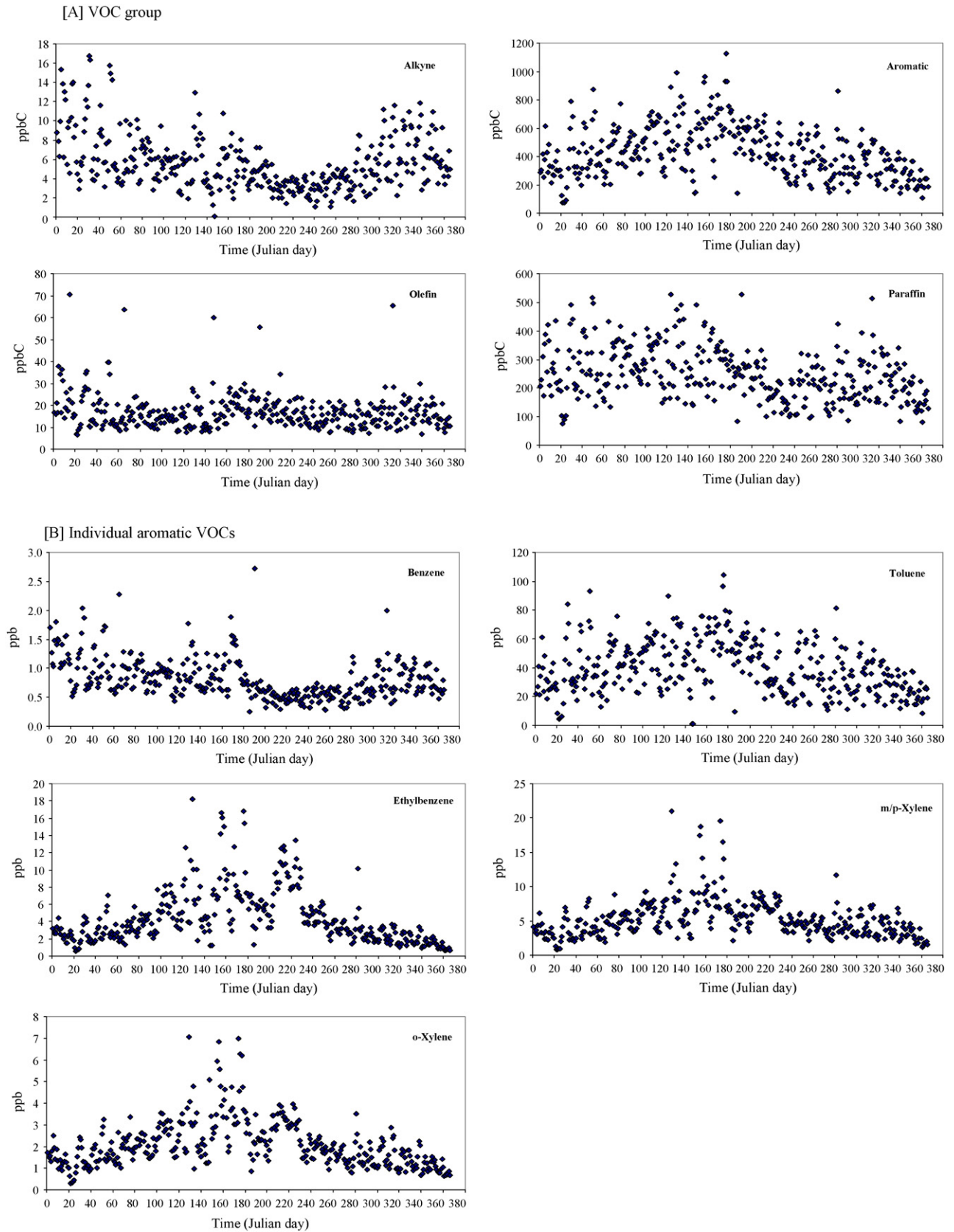


Fig. 4. The daily variation of VOCs at Sung-Su, Seoul, Korea (2004).

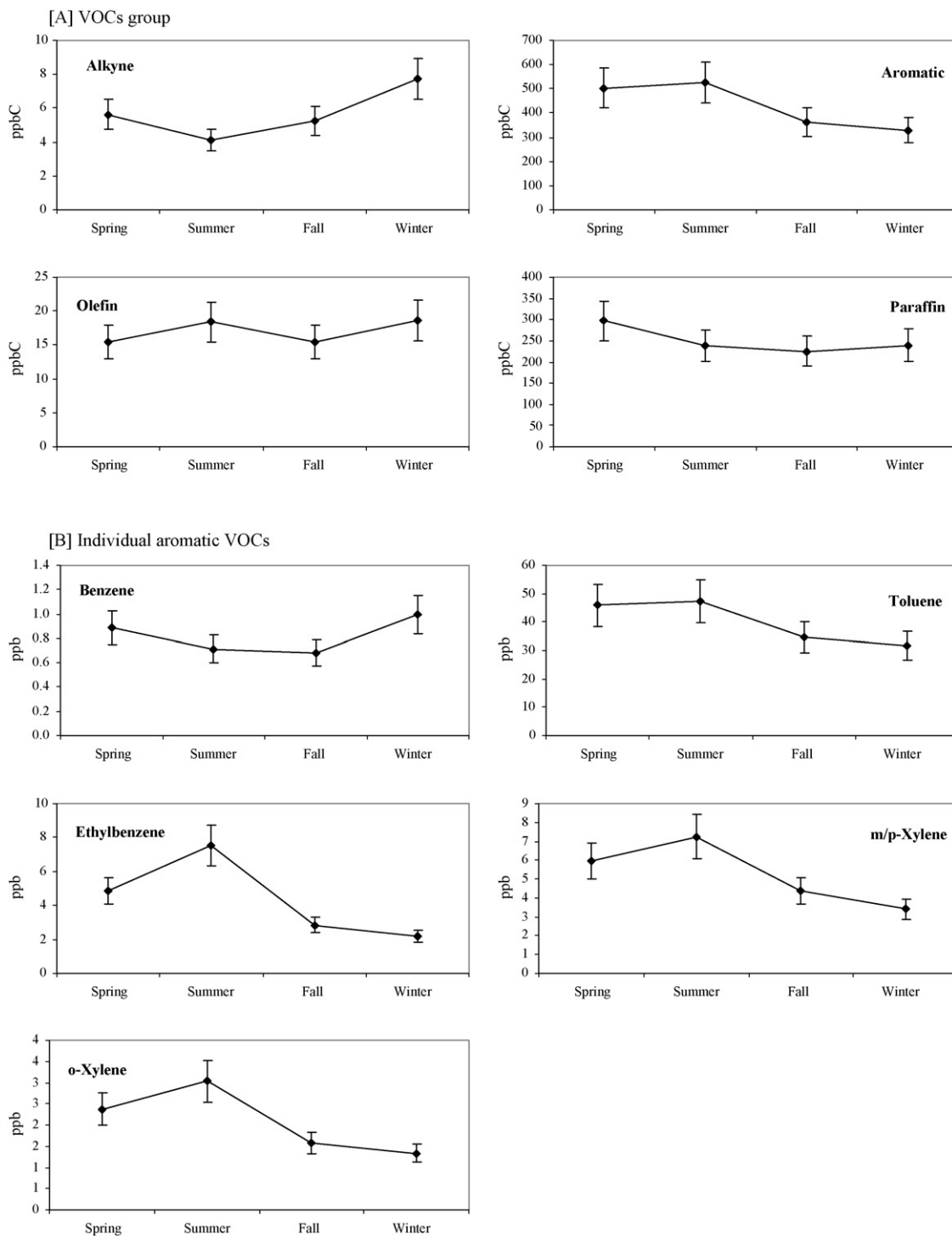


Fig. 5. Comparison of the seasonal mean values for the VOCs.

### 3.4. Factors affecting VOC distributions in the study area

Correlation analyses based on data collected daily aided the evaluation of factors controlling the behavior of VOCs such as: between VOC groups and individual VOC components as well as between VOCs and relevant meteorological parameters. As shown in Table 3, correlations between different data pairs were compared by means of the magnitude of probability ( $P$ ). All results were arbitrarily divided into the four following classes based on

their correlation strengths: (1) no class (the weakest correlation strength range):  $P \geq 10^{-2}$ ; (2) class I:  $10^{-5} \leq P < 10^{-2}$ ; (3) class II:  $10^{-10} \leq P < 10^{-5}$ ; (4) class III:  $10^{-20} \leq P < 10^{-10}$ ; and (5) class IV (the strongest correlation range):  $P < 10^{-20}$ .

The results of the correlation analysis showed that strongly correlated cases (e.g., classes III and IV relative to classes I and II) covered up to 66% of all matching pairs. The strongest correlation (class IV) was largely in the AR or PR groups, while some individual species like (toluene and *o*-xylene) also exhibited a high level of



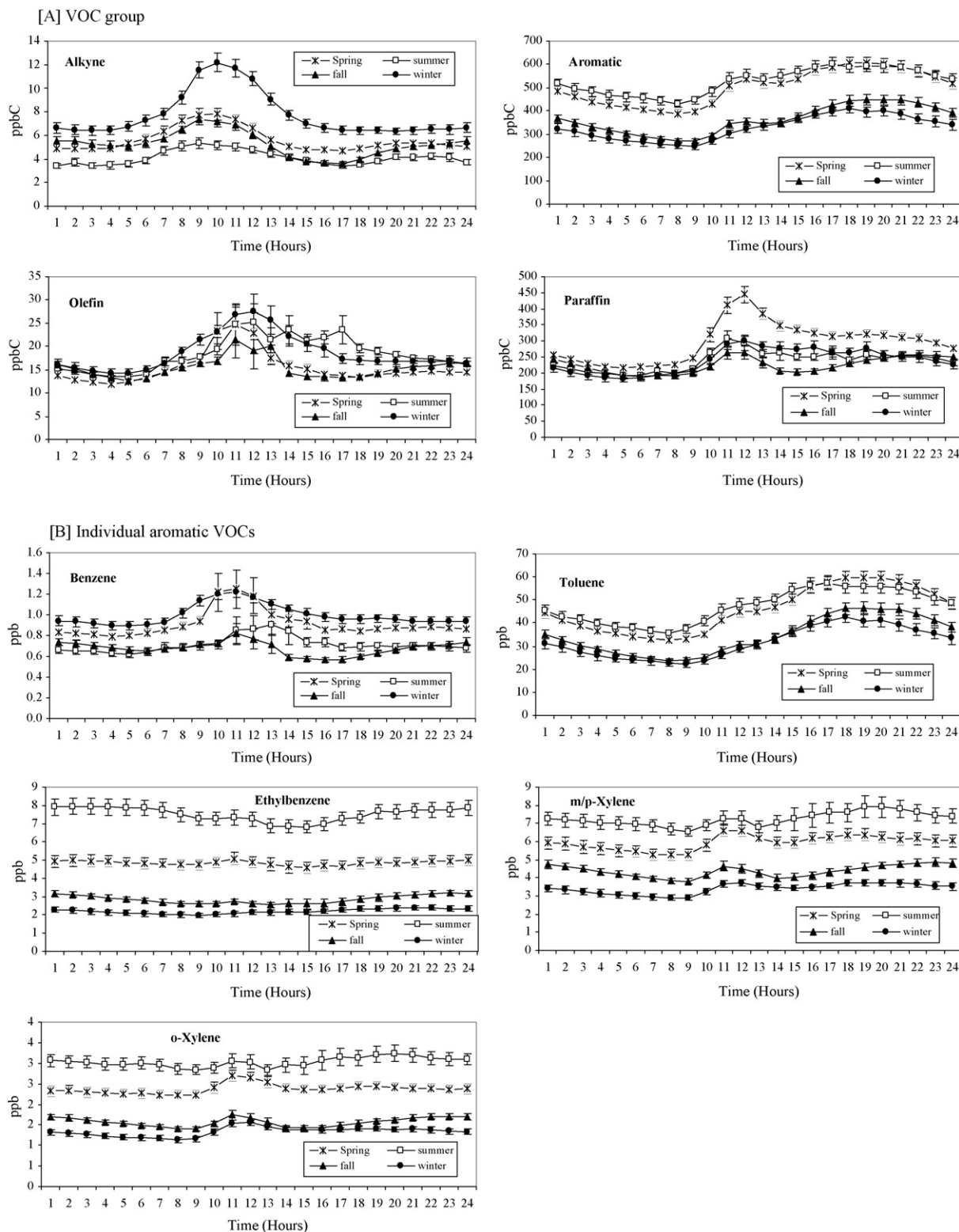


Fig. 6. Diurnal variation patterns of VOCs over different seasons from the Sung-Su station in 2004 (S.D. shown as error bar).

correlation with other species. Our analyses indicate the existence of a certain pattern in which enhanced correlation strengths can be seen for some matching pairs with relatively high concentrations. The existence of strong correlations between individual VOCs may be explained largely due to the similar chemical properties for a given chemical group (e.g., aromatic group). On the other hand,

the relatively strong correlation pairs were seen only sporadically between the VOCs and the meteorological parameters (e.g., 25% of the matching pairs).

The correlation analyses for VOCs and meteorological parameters showed that strong correlation pairs were lacking for most matching pairs. There were, however, 3 cases of strong correlation

**Table 4**  
Compilation of VOC concentration data measured between different studies

VOC No.	Compound	Ref. No. (country) <sup>a</sup>							
		1	2	3	4	5	6	7	8
		Korea	Korea	UK	Australia	US	China	Pakistan	Chile
[A] Comparison of concentration levels of individual VOC (in ppb)									
1	Ethane	3.85	3.8	4.25	7.5	6.4	10.35	93	9.4
2	Ethylene	1.73		2.62					
3	Propane	9.57	7.8	4.06	5.9	3.2	11.15	41	137.5
4	Propylene	2.12		7.11					
5	Isobutane	3.16							
6	<i>n</i> -Butane	5.37		3.59	7.5	6	7.55	19.8	27
7	Acetylene	2.84		4.14				18.0	
8	<i>trans</i> -2-Butene	0.36		0.26			1.71	0.3	
9	1-Butene	0.22	0.5	0.2	1		1.24	1.1	2.4
10	<i>cis</i> -2-Butene	0.22	0.2	0.14			1.36	0.2	
11	Cyclopentane	1.22	0.3						
12	Isopentane	2.24							
13	<i>n</i> -Pentane	1.2		0.75	5	3.8	3.95	13.4	6.6
14	<i>trans</i> -2-Pentene	0.19	0.2	0.16			2.66	0.3	
15	1-Pentene	0.11							
16	<i>cis</i> -2-Pentene	0.1	0.2	0.09			4.71	0.1	
17	2,2-Dimethylbutane	0.3	0.1				0.2	0.4	
18	2,3-Dimethylbutane	0.28	0.5				2.51	0.5	
19	2-Methylpentane	0.14	0.9		2.6	2.4	2.84	4.7	4.8
20	3-Methylpentane	0.13	0.2		1.6	2.4	1.85	3.1	2.8
21	Isoprene	0.34	0.3	0.12				0.8	0.5
22	1-Hexene	0.05							
23	<i>n</i> -Hexane	3.3		0.34	2.1	2	1.65	7.5	4.1
24	Methylcyclopentane	4.38	1.1						
25	2,4-Dimethylpentane	6.98	0.1					0.3	
26	Benzene	0.82	1	1.1	2.6	2.4	5.55	5.2	6
27	Cyclohexane	1.57	0.5						
28	2-Methylhexane	0.43	0.3					1.8	
29	2,3-Dimethylpentane	0.16	0.4						
30	3-Methylhexane	0.44	0.5						
31	2,2,4-Trimethylpentane	0.45						0.5	
32	<i>n</i> -Heptane	0.6		0.14			1.73	3.9	2.8
33	Methylcyclohexane	0.54	0.4						
34	2,3,4-Trimethylpentane	0.15							
35	Toluene	39.8	6.4	2.12	8.9	3.8	5.8	7.1	21.8
36	2-Methylheptane	1.71	0.2						
37	3-Methylheptane	1.2	0.2						
38	<i>n</i> -Octane	0.31					0.67	1.1	1.1
39	Ethylbenzene	4.35	0.7	0.46			1.4		
40	<i>m/p</i> -Xylene	5.25	2.3	1.35	2.3	1.5	7.85	3.1	10.3
41	Styrene	0.51	0.3					0.4	
42	<i>o</i> -Xylene	2.08	0.8	0.55	1.5	0.4	3.5	1.1	3.8
43	<i>n</i> -Nonane	1.52					0.37	0.7	
44	Isopropylbenzene	0.68							
45	<i>n</i> -Propylbenzene	0.25					0.16	0.2	
46	<i>m</i> -Ethyltoluene	0.65							
47	<i>p</i> -Ethyltoluene	0.37							
48	1,3,5-Trimethylbenzene	0.69	0.3				0.57	0.4	
49	<i>o</i> -Ethyltoluene	0.32	0.8						
50	1,2,4-Trimethylbenzene	1.07			1.3		1.5	1	3.1
51	<i>n</i> -Decane	2.31					0.22	0.7	
52	1,2,3-Trimethylbenzene	0.9							
53	<i>m</i> -Diethylbenzene	0.24							
54	<i>p</i> -Diethylbenzene	0.3							
55	<i>n</i> -Undecane	1.1							
56	<i>n</i> -Dodecane	0.61							
Ref. No.	1	2	3	4	5	6	7	8	
[B] References									
City	Seoul	Seoul	12 cities	Sydney	Chicago	43 cities	Karachi	Santiago	
Country	Korea	Korea	UK	Australia	US	China	Pakistan	Chile	
Author	This study	Na and Kim	Derwent et al.	Nelson et al.	Aronian et al.	Barletta et al.	Barletta et al.	Chen et al.	
Publication year		2001	2000	1982	1989	2005	2002	2001	
Measurement year	January 2004 to December 2004	August 1998 to July 1999	January 1996 to December 1996	Unknown	Unknown	January 2001 to February 2001	During winter of 1998–1999	June 1 and June 8, 1996	
Number of measurement data	17–8656	Unknown	4411–7525	Unknown	Unknown	Unknown	Unknown	Unknown	
Note				Shown in Barletta et al. (2002)	Shown in Barletta et al. (2002)	Average taken from the minimum and maximum values from 43 cities		Shown in Barletta et al. (2002)	

<sup>a</sup> Refer to part B of this Table for more information about individual references.

pairs (class IV). All of these cases were related to temperature for the following VOCs: ethylbenzene, *m/p*-xylene, and *o*-xylene. Thus, most strongly correlated cases appeared mainly with temperature. Such patterns were also found from a few VOC groups (AK and AR group; class III). The results of this comparison thus confirmed that temperature may exert a significant influence on the distribution of VOCs either in a group or as individual components. In addition, UV is also found to share fairly strong correlations with VOCs, e.g., the AK group and certain individual species (e.g., ethylbenzene and *o*-xylene) (class III). In comparison, a strong correlation was not observable between relative humidity and individual VOC (and PR group).

### 3.5. Comparison with previous studies

Our measurement data were compared with the results of previous studies to evaluate VOC concentration levels in terms of geographical criterion (Table 4). Large VOC data sets measured from other countries were collected and summarized in a consistent manner. According to this comparison, many data sets from different studies exhibited similarities and dissimilarities. The highest VOC value (138 ppb) was observed from propane in Santiago, Chile [30] followed by ethane (93 ppb) in Karachi, Pakistan [31] and toluene in this study (39.8 ppb). However, as shown in Table 4, the concentration levels of most VOCs were generally below 20 ppb.

To facilitate the comparison of VOC concentration levels between different study groups, the original data for individual species reported in other studies (in ppb unit) were also bound together for the derivation of VOC functional group (ppbC unit). The differences in the mixing ratios of the AR and PR groups were significantly large in such countries as Pakistan and Chile. It should be noted that the leakage of unburned LPG caused significant emissions of PR groups (e.g., propane and butane) into the air of both Santiago (Chile) and Karachi (Pakistan) [30,31]. In fact, the LPG leakage was estimated to contribute to as much as 15% of the excess ozone levels in Santiago (Chile) [30]. Emissions from vehicular exhaust were also reported to be an important source in Karachi (Pakistan) [31]. The lowest mixing ratios for the AR group were recorded from 12 cities in the UK with a mean of 40.4 ppbC [15]. However, the highest value (430 ppbC) was observed in Seoul. The highest mixing ratios for the PR group (671 ppbC) were found in Santiago, Chile [30] followed by Karachi, Pakistan (621 ppbC; Barletta et al. [31]), and Sung-Su, Seoul (250 ppbC). In contrast, the lowest mixing ratio for PR was observed in the UK with a mean of 41.8 ppbC [15]. However, the data for the AK and OF groups were not available in some studies (e.g., the absence of the former in Na and Kim [13] and the latter in Aronian et al. [32]). The highest mixing ratio of the OF group was 54.1 ppbC in 43 cities in China [33], while its lowest value (4.0 ppbC) occurred in Sydney, Australia [34].

A comparison of the individual BTEX component indicated that the toluene concentration levels were the highest in most studies. Additionally, notably higher concentration levels of toluene such as 39.8 (Seoul: the present study) and 21.8 ppb (Santiago: Chen et al. [30]) were also recorded. There were exceptions, as seen in 43 cities in China [33]. The highest mixing ratio in China was *m/p*-xylene (7.85 ppb). Nonetheless, differences in the concentration levels between individual VOC components were not significant. VOC concentration levels in most urban environments were of similar magnitude among different chemical groups and/or compounds.

## 4. Summary

As part of the PAMS program, a total of 56 VOCs were measured at the PAMS type III monitoring site in the Sung-Su district

of Seoul, Korea in 2004. The highest VOC concentration value was recorded by toluene (39.8 ppb), while the lowest concentration value by 1-hexene (0.05 ppb). The concentration levels of the VOC functional groups showed the highest concentration for the AR group (430 ppbC), while the lowest mean value was found for the AK group (5.68 ppbC). This may be because the SS site is located near an area with heavy traffic and surrounded by a multitude of local manufacturing facilities.

Examination of seasonal data sets indicated that AK and OF concentrations generally peaked during winter, while the AR group peaked during summer. The diurnal variation patterns of the VOCs also indicated that the concentrations of most VOC groups (e.g., AK, OF, and PR) peaked around midday. In contrast, as the emissions due to evaporation and traffic activities influence the diurnal variation patterns of AR, their peaks were generally seen in the late afternoon period. However, the analysis of diurnal patterns for individual aromatic components showed a contrasting pattern between toluene and benzene; toluene occurred more at night, while benzene occurred during noontime in all four seasons. In addition, the relative dominance of toluene can be explained at least partially by significantly high traffic activities in the evening time. The results of correlation analyses indicated that the strongly correlated pairs occurred mostly between the AR group and individual BTEX components. As for the relationship between VOCs and environmental parameters significant correlations were observed scarcely with the exception of temperature (e.g., with some BTEX). This confirms that temperature is one of the most sensitive environmental parameters affecting the distribution of aromatic VOCs.

A comparison of the VOC concentration levels between different studies revealed that the leakage of LPG fuels often caused exceedingly high mixing ratios of certain VOCs in certain countries. The results of this research suggest that anthropogenic emissions have contributed greatly to increases VOC pollution levels at the study site, as it is surrounded by a large number of man-made activities. The changes in meteorological conditions can exert noticeable influences on their temporal distributions of VOCs at varying temporal scales such as over the diurnal and seasonal intervals. Because VOC pollution is significant in certain urban locations such as our target study area, concerted efforts are needed to place limits on VOC emissions from various source processes. Also, technical improvements in fuel quality aided by legislative controls on emissions will help decrease the pollution levels of VOCs in ambient air.

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