

# The Relative Importance of Indoor and Outdoor Sources for Determining Indoor Pollution Concentrations in Homes in Seoul, South Korea

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## ABSTRACT

This study measured indoor and outdoor levels of hydrocarbon volatile organic compounds (VOCs), such as benzene, toluene, ethylbenzene, and xylene isomers (collectively referred to as BTEX), as well as 13 carbonyl compounds, at 20 homes in Seoul, South Korea. Along with the sampling of BTEX and carbonyls, indoor concentrations of the air pollutants nitrogen oxide (NO) and carbon dioxide (CO<sub>2</sub>) were also measured at each home. These measurements were used to understand the characteristics of BTEX and carbonyls by calculating the various ratios and correlation coefficients between measured contaminant levels. We found that carbonyls were mostly originated from indoor sources, while BTEX were originated from both indoor and outdoor sources. A high correlation between indoor levels of NO and BTEX indicated that traffic emissions were also an important sources of BTEX.

**Key words:** Volatile organic compound, Aromatic hydrocarbon, Carbonyl compound, Indoor air pollutant, BTEX, Indoor-to-outdoor ratio, Positive matrix factorization

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## 1. INTRODUCTION

Volatile organic compounds (VOCs) and carbonyl compounds emitted into the atmosphere have been studied due to their adverse impacts on human health. Previous studies have found that concentrations of these organic chemicals are higher indoors than outdoors (Bruno *et al.*, 2008; Jia *et al.*, 2008; Parra *et al.*, 2008; Báez *et al.*, 2003; Guo *et al.*, 2003). Human exposure to

VOCs and carbonyls via inhalation is directly related to indoor concentrations because people spend more time in indoor environments. Studies have therefore focused on indoor emissions and transport of VOCs and carbonyl compounds to understand the effects of these compounds on human health.

Among VOCs, aromatic hydrocarbons, such as benzene, toluene, ethylbenzene, and xylenes (collectively referred to as BTEX), mainly emitted from petroleum and natural gas combustion, are well-known for their carcinogenicity and abundance in indoor environments (Kume *et al.*, 2008; Skov *et al.*, 2001). Previous studies have investigated the correlations between indoor BTEX levels and various factors. Schlink *et al.* (2010) found that indoor VOC concentrations were strongly correlated with seasonality and residence type. They also reported high levels of benzene, toluene, and xylene isomers in apartments adjacent to highly trafficked roadways. Buczynska *et al.* (2009) determined that traffic jams due to merging lanes increased BTEX concentrations in Antwerp, Belgium. Guo *et al.* (2003) reported that indoor BTEX concentrations in several microenvironments were related to automobile exhaust, cooking style, type of gas stove, and cigarette smoking. In a study by Ilgen *et al.* (2001), traffic density was a key factor in determining indoor BTEX concentrations in urban areas, while indoor sources of BTEX were important in rural areas.

Carbonyl compounds emitted from automobile exhausts, building and furnishing materials, cigarette smoking, and consumer products have also been studied, as they can cause discomfort and irritation to human organs (Liu *et al.*, 2013; Marchand *et al.*, 2006; Zhang *et al.*, 1994). Among carbonyls, formaldehyde and acetaldehyde have been classified as toxic and carcinogenic compounds by the International Agency for Research

on Cancer (IARC, 2004) and the U.S. Environmental Protection Agency (EPA, 1989). Due to the adverse health effects of these chemicals, previous studies have mainly focused on indoor and outdoor concentrations and the factors affecting these levels. Sakai *et al.* (2004) found a link between the airtight designs of newer dwellings and higher formaldehyde concentrations. Báez *et al.* (2003) showed that levels of formaldehyde and acetaldehyde were related to the presence of smokers, and Liu *et al.* (2013) found that urban areas in the U.S.A. had the highest levels of indoor sources. According to Kim *et al.* (2013), relative humidity is also associated with indoor concentrations of formaldehyde, and furniture and the age of the interior are major factors in formaldehyde levels in libraries and private reading rooms.

Although there are many previous studies, which investigated the characteristics of BTEX and carbonyls worldwide, no previous studies to our knowledge were conducted in South Korea. This study investigated the characteristics of BTEX and carbonyls at 20 homes in Seoul, South Korea, to understand the properties and the relative importance of indoor and outdoor sources of these compounds. In order to understand the origin of these pollutants, we calculated various ratios and correlation coefficients between measured concentration levels, such as indoor to outdoor ratios of BTEX and carbonyls.

## 2. MATERIALS AND METHODS

### 2.1 Sampling Sites and Methods

#### 2.1.1 BTEX and Carbonyl Compounds

Samples were taken at 20 homes near heavily trafficked roads in Seoul, South Korea, on workdays from November 2013 to December 2014. The geographical information of measurement sites were shown in Fig. S1 in the supplementary material. Indoor and outdoor air samples were collected simultaneously from both the middle of the living room and the balcony for high-rise apartments. For low-story buildings, outdoor VOC and carbonyl measurements were taken in the front yard of the house. Indoor and outdoor sampling was conducted at each home an average of four times over 48 hours (totaling eight samples for each VOC and carbonyl, including both indoor and outdoor measurements). We chose 48 hours as the measurement period, because it was long enough to measure the concentrations several times but not too long to keep people from volunteering for the study. All VOC and carbonyl measurements were undertaken during the day. Table 1 shows the general features of the homes and residents.

VOCs were collected in Tenax TA adsorbent tubes

(APK-1200, KnR, Korea) for 30 minutes using a personal pump (GilAir Plus, Gilian, USA) at a flow rate of 125 to 135 mL/min during the day. Prior to each sampling, every Tenax TA tube was cleaned with an ultra-pure nitrogen gas flow of 50 mL/min at a temperature of 300°C for three hours, to remove any contamination. After sampling, the sealed Tenax TA tubes were immediately stored in a refrigerator at less than 4°C until analysis.

For carbonyl compounds, DNPH-Silica cartridges (LpDNPH S10, Supelco Inc., USA) equipped with ozone scrubbers (LpDNPH, Supelco Inc., USA) were used. Carbonyls were collected into cartridges with a personal pump (GilAir Plus, Gilian, USA) at a flow rate of 500 mL/min for 30 minutes. The ozone scrubber was connected to the upstream end of the cartridge, and the personal pump was connected to the downstream end. After sampling, the cartridges were tightly sealed, wrapped with aluminum foil, and stored in a refrigerator until analysis.

Residents were also questioned about five possible indoor sources of BTEX and carbonyl emissions: interior renovations within the last two years, the purchase of new furniture and/or consumer products, cigarette smoking, frequency of dry cleaning, and printer usage. During the measurement period, all occupants acted, and ventilated their house, as normal.

#### 2.1.2 NO and CO<sub>2</sub>

To measure indoor NO concentrations in the homes, a Model 42i NO-NO<sub>2</sub>-NO<sub>x</sub> Analyzer (Thermo Scientific, USA) was used. For indoor CO<sub>2</sub> measurements, a 1370 NDIR CO<sub>2</sub> Analyzer (TES, Taiwan) was used. The instruments reported the real-time concentrations every 60 seconds. The NO and CO<sub>2</sub> measurement systems were placed on an experimental tray, positioned between the living room and the kitchen, 1 m above the floor.

### 2.2 Analytical Methods

Six VOC compounds, including benzene, toluene, ethylbenzene, and xylenes (*m*-, *p*-, and *o*-xylenes), were analyzed based on the ISO 16000-6 method. The samples were analyzed using an automated thermal desorption-gas chromatography-mass spectrometry (ATD-GC-MS) method. VOCs were desorbed from Tenax TA tubes with an ultra-pure nitrogen gas flow of 50 mL/min at 300°C for 10 minutes using a thermal desorber (TurboMatrix ATD 350, Perkin Elmer, USA). Subsequently, the VOC samples were analyzed using a Hewlett-Packard 6890 gas chromatograph equipped with a 5973 mass spectrometer (GC-MS, HP, Palo Alto, CA, USA). A ZB-1ms capillary, 60 m in length, 0.25 mm inner diameter (i.d.), and 1 μm thickness (ZB-1, Phenomenex, USA)

**Table 1.** General description of sampled homes and their residents.

Home	Time of the year	Home type	Home age (yr)	Floor number	Home size (m <sup>2</sup> )	Stove type	Number of occupants	Number of smokers
Home 1	2013.09.30-10.02	High-rise	13	19	85	Gas	4	0
Home 2	2013.11.19-11.21	Low-rise	20	1	90	Gas	4	0
Home 3	2013.12.03-12.05	High-rise	4	25	84	Gas	4	0
Home 4*	2014.01.06-01.07	High-rise	7	18	109	Gas	3	0
Home 5	2014.01.21-01.23	High-rise	13	19	85	Gas	4	0
Home 6	2014.02.04-02.06	High-rise	13	4	185	Gas	4	0
Home 7	2014.02.18-02.20	High-rise	4	25	80	Gas	4	0
Home 8	2014.02.24-02.26	High-rise	15	2	80	Gas	2	0
Home 9	2014.03.11-03.13	High-rise	21	5	75	Gas	4	1
Home 10	2014.03.17-03.19	High-rise	26	8	117	Gas	4	0
Home 11	2014.04.01-04.03	High-rise	26	15	85	Gas	4	0
Home 12	2014.05.13-05.17	High-rise	17	1	50	Electric	3	0
Home 13	2014.07.14-07.16	High-rise	17	6	50	Gas	3	0
Home 14	2014.07.29-07.31	Low-rise	20	2	50	Gas	3	0
Home 15	2014.08.06-08.08	Low-rise	20	3	100	Electric	4	0
Home 16	2014.08.11-08.13	High-rise	2	14	85	Electric	4	0
Home 17 <sup>†</sup>	2014.09.17-09.19	High-rise	38	9	87	Gas	3	0
Home 18	2014.11.04-11.06	High-rise	7	24	108	Gas	4	0
Home 19	2014.11.18-11.20	High-rise	23	2	86	Gas	3	0
Home 20	2014.12.02-12.04	High-rise	15	25	51	Gas	4	0

\*Measurements were performed for only 24 hours at the request of the residents.

<sup>†</sup>Carbonyl concentration measurements were eliminated due to sampling error.

was used for chromatographic separation. The oven temperature of the gas chromatograph was initially held at 40°C for four minutes, and then raised to 250°C at a rate of 6°C/min. Subsequently, it was raised at a rate of 10°C/min, and a final temperature of 300°C was reached and then held for 6 minutes. The total retention time in the gas chromatograph was therefore 50 minutes. TVOC concentrations were calculated based on the sum of C<sub>6</sub>-C<sub>16</sub> concentrations and toluene calibration curve.

The 13 carbonyl compounds analyzed were formaldehyde, acetaldehyde, acrolein, acetone, propionaldehyde, crotonaldehyde, methacrolein, 2-butanone, butyraldehyde, benzaldehyde, valeraldehyde, m-tolualdehyde, and hexaldehyde. Since it was difficult to quantify the concentrations of acrolein and acetone separately due to their chromatographic co-elution, we quantified the sum of the two compounds. Compounds contained in cartridges were eluted with 5 mL of acetonitrile in high performance liquid chromatography (HPLC)-grade water (ACN, J.T. Baker, USA) using a 10-mL syringe connected to a cartridge adaptor. Subsequently, the extracts were analyzed using the HPLC method with an injection volume of 20 µL into the liquid chromatograph. A UV/diode-array detector (DAD) was used for this process, and the derivatives were detected at 360 nm. A YMC-Pack ODS-A column of 5 µm × 25 cm × 4.6 mm was used, with a column oven temperature of 25°C. The volume ratio of water to acetonitrile was 60 : 40.

### 2.3 Quality Assurance and Control

Field blanks were prepared to check the background levels of chemicals, and to detect any contamination during sample handling, storing, and analysis. The field blanks consisted of one or two tubes and cartridges for each home measurement. By using the mean and standard deviation of the concentration levels in the field blanks, the detection limits (mean+3σ) for all compounds were obtained (see Tables S1 and S2 in the supplementary material). The values of the field blanks were subtracted from those of the measurement samples.

BTEX compounds were calibrated using standard mixtures (Indoor Air Standard, 50 Component, Supelco Inc., USA) with the concentration range of the compounds from 0 to 200 ng/µL. A 5-point calibration curve was prepared to quantify the BTEX compounds in the samples. A certified calibration mix standard (Carb Method 1004 DNPH Mix 2, Supelco, USA) was also used for the 13 carbonyls, whose concentrations ranged from 0 to 300 ng/mL. In the carbonyl compound calibration, a 6-point calibration curve was prepared. For MS detection, quality control was performed on every 9<sup>th</sup> sample, using standard mixtures including hexane (100 ng/µL), toluene (50 ng/µL), decane (50 ng/µL), tetradecane (50 ng/µL), pentadecane (50 ng/µL), and hexadecane (50 ng/µL) in a volume of 2 µL. The percentages of recovery were all higher than 96%.

**Table 2.** Descriptive statistics for the measured indoor and outdoor BTEX and carbonyl concentrations.

	(in $\mu\text{g}/\text{m}^3$ )	N	Mean	Std. dev.	Median	Max	Min
Indoor	Benzene	73	3.39	7.07	1.95	53.89	<LOD
	Toluene	73	39.77	45.43	26.08	253.94	<LOD
	Ethylbenzene	73	7.75	13.04	4.60	103.82	<LOD
	Xylenes	73	10.17	12.61	6.46	54.21	<LOD
	BTEX	73	61.08	65.02	36.55	370.08	<LOD
	TVOC	73	989.20	3120.01	285.77	22954.38	3.43
	Formaldehyde	78	27.68	16.32	24.26	81.10	0.20
	Acetaldehyde	78	11.53	7.21	10.16	48.70	1.06
	Carbonyls*	78	106.82	72.92	94.10	474.10	0.20
Outdoor	Benzene	73	3.75	7.69	1.64	47.12	<LOD
	Toluene	73	28.69	37.15	15.71	213.07	<LOD
	Ethylbenzene	73	4.29	4.89	2.82	24.27	<LOD
	Xylenes	73	5.76	7.32	3.22	34.89	<LOD
	BTEX	73	42.49	50.55	28.45	276.19	0.89
	TVOC	73	306.03	555.67	102.37	3532.60	1.39
	Formaldehyde	78	7.31	6.98	4.87	38.10	<LOD
	Acetaldehyde	78	4.83	4.88	3.68	26.95	<LOD
	Carbonyls*	78	32.75	20.89	29.08	92.16	<LOD

\*Carbonyls include formaldehyde and acetaldehyde.

## 2.4 Statistical Analysis

First, the I/O ratios and correlations between indoor and outdoor levels were calculated to establish the origin (indoor or outdoor) of indoor BTEX and carbonyl compounds. Next, the correlations between these compounds and indoor air pollutants were analyzed. The indoor air pollutants investigated were nitrogen oxide (NO), one of the oxides of nitrogen, and carbon dioxide (CO<sub>2</sub>), selected because CO<sub>2</sub> concentration can be used as an indicator of ventilation and occupancy levels (Bentayeb *et al.*, 2013; Jia *et al.*, 2008), while NO concentration can indicate traffic volumes (Vardoulakis *et al.*, 2002). Additionally, correlations of BTEX and carbonyl compounds with possible indoor sources, such as interior materials, new furniture, cigarette smoke, high frequency of dry cleaning, and printer usage, were investigated. The ratios of toluene-to-benzene and formaldehyde-to-acetaldehyde were also calculated for further assessment of the characteristics of the organic chemicals in this study. Lastly, positive matrix factorization (US EPA PMF version 5.0) was performed on the measured indoor and outdoor BTEX concentrations to enable apportionment of the sources.

## 3. RESULTS AND DISCUSSION

### 3.1 Indoor and Outdoor Levels of BTEX and Carbonyls at Homes

Table 2 shows the descriptive statistics for the measured indoor and outdoor concentrations of BTEX for 20 homes, and of carbonyl compounds for 19 homes.

The total number of samples was 73 for BTEX and total VOC (TVOC) concentrations, including from C<sub>6</sub> to C<sub>16</sub>, and 78 for carbonyls (approximately four times per home). Of the indoor and outdoor BTEX samples, toluene had the highest concentrations, followed by xylenes, ethylbenzene, and benzene. The average indoor BTEX concentration was 1.46 times higher than the outdoor concentration, while the average indoor TVOC and carbonyl concentrations were both more than 3 times higher than the outdoor concentrations. In a study by Kim *et al.* (2013), which investigated indoor aldehyde concentrations in South Korea, they detected similar concentrations of formaldehyde (29.2  $\mu\text{g}/\text{m}^3$ ) and acetaldehyde (8.9  $\mu\text{g}/\text{m}^3$ ) in a public library, while much higher aldehyde concentrations were detected in a children's library, and in public and private reading rooms. Note that the mean indoor and outdoor concentrations of benzene were below ambient air pollution guideline concentrations for South Korea (5  $\mu\text{g}/\text{m}^3$ ) (MOE, 2016), but above Japan's guideline (3  $\mu\text{g}/\text{m}^3$ ) (MOE, 2016). The indoor and outdoor mean concentrations of formaldehyde were much lower than indoor air pollution guideline concentrations, which are 100  $\mu\text{g}/\text{m}^3$  both for Korea (Kim *et al.*, 2013) and the WHO (WHO, 2000).

Table 3 shows the indoor and outdoor concentrations and I/O ratios of BTEX and carbonyls for each home. Also shown are average concentrations, average I/O ratios, and correlation coefficients between indoor and outdoor concentrations of BTEX and carbonyls. For BTEX concentrations, I/O ratios were mostly greater than 1, except for three homes (homes 6, 10, and 14). The average I/O ratio of the 20 homes for BTEX was

**Table 3.** Indoor and outdoor concentrations, I/O ratios, and correlation coefficients for BTEX and carbonyls.

(in $\mu\text{g}/\text{m}^3$ )	BTEX			Carbonyls		
	Indoor	Outdoor	I/O ratio	Indoor	Outdoor	I/O ratio
1	56.84	52.60	1.08	52.80	31.13	1.70
2	36.13	33.28	1.09	88.80	21.41	4.15
3	142.47	103.06	1.38	181.90	47.28	3.85
4	191.58	131.47	1.46	177.82	31.91	5.57
5	60.18	47.00	1.28	64.35	25.56	2.52
6	22.73	35.95	0.63	82.87	20.41	4.06
7	106.27	26.69	3.98	123.80	36.90	3.35
8	69.44	54.49	1.27	121.04	27.49	4.40
9	42.52	34.34	1.24	123.04	57.20	2.15
10	10.85	11.28	0.96	67.80	10.97	6.18
11	161.32	109.35	1.48	306.11	43.45	7.04
12	50.89	19.60	2.60	98.71	25.75	3.83
13	12.43	11.46	1.08	93.45	57.61	1.62
14	11.84	12.35	0.96	47.58	32.04	1.48
15	56.43	30.13	1.87	74.75	29.24	2.56
16	82.45	71.52	1.15	75.83	50.03	1.52
17	71.35	48.35	1.48	—*	—*	—*
18	64.82	27.16	2.39	115.37	42.22	2.73
19	32.40	18.40	1.76	78.42	25.69	3.05
20	32.74	8.62	3.80	101.21	13.18	7.68
Average	61.08	42.49	1.44	106.82	32.75	3.26
I & O correlation coefficient		0.91			0.34	

\*Carbonyl concentration measurements were eliminated due to sampling error.

1.44. The average I/O ratios for benzene, toluene, ethylbenzene and xylenes at six homes in Hong Kong were 2.566, 1.617, 0.505 and 1.039, respectively (Guo *et al.*, 2003), while that for BTEX at 352 homes with one-year old children in Valencia, Spain was 2.41 (Esplugues *et al.*, 2010). The correlation between indoor and outdoor BTEX was 0.91 (see Table S3 for the significance of the correlation).

In all homes sampled for carbonyl concentrations, all I/O ratios were higher than 1. The average I/O ratio for all 19 homes was 3.26, which was higher than that for the BTEX samples. The highest I/O ratio, 7.68, was observed at home 20, probably due to renovations and the purchase of new furniture and consumer products within the last two years. The correlation coefficient between indoor and outdoor carbonyls was 0.34, which was smaller than that for BTEX (see Table S3 for the significance of the correlation).

In general, an I/O ratio greater than 1 indicates the existence of indoor sources of compounds. On the other hand, a correlation coefficient close to 1 indicates that indoor pollutants are mainly infiltrating from outdoors, while a correlation coefficient close to 0 implies primarily indoor sources of contaminants. In this study, an I/O ratio of 1.44 and a high correlation coefficient of 0.91 for BTEX indicate that both indoor sources and infiltra-

tion of outdoor air have affected indoor pollutant levels. However, for carbonyls, a high I/O ratio of 3.26 and low correlation coefficient of 0.34 indicate that indoor sources were the primary contributor to indoor levels. Possible indoor pollutant sources of BTEX and carbonyls include interior materials, new furniture and consumer products, cooking style, type of stove, cigarette smoking, frequency of dry cleaning, and printer usage, whereas possible outdoor sources of BTEX include traffic emissions.

### 3.2 Correlation of BTEX and Carbonyl Concentrations with NO and CO<sub>2</sub> Concentrations

To determine whether a correlation existed between BTEX or carbonyl levels and other indoor pollutants, NO and CO<sub>2</sub> concentrations were measured. NO measurements were conducted at 14 of the 20 homes, and CO<sub>2</sub> measurements at 19 of them. Fig. 1 shows the average indoor NO and BTEX concentrations at each home, indicating that BTEX concentration increased with an increase in NO concentration. The correlation coefficient was 0.67, as shown in Table 4. This high degree of correlation is probably due to both nitrogen oxides and BTEX having been identified as indicators of traffic emissions in previous studies (Yamada *et al.*, 2011;



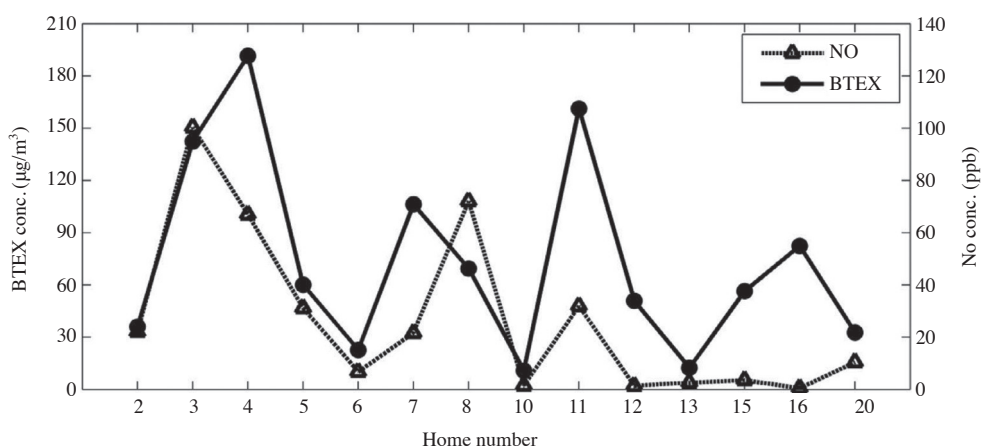


Fig. 1. Average indoor NO and BTEX concentrations at each home.

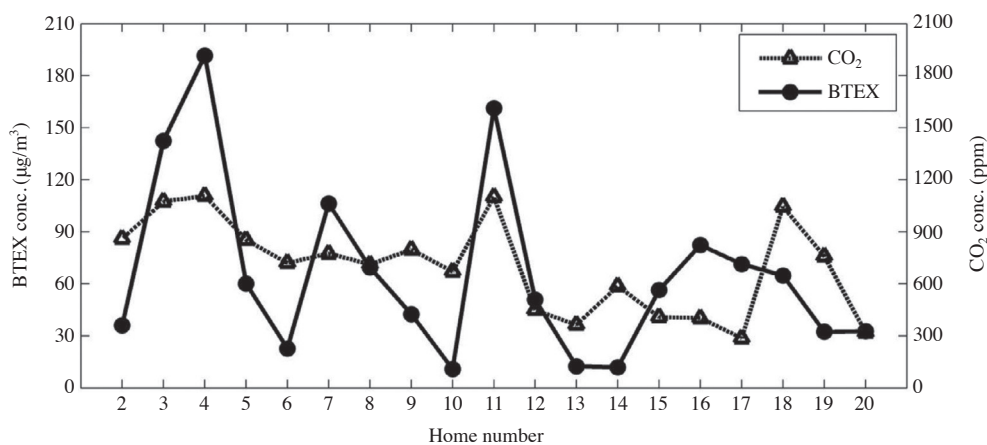


Fig. 2. Average CO<sub>2</sub> and BTEX concentrations at each home.

Zalel *et al.*, 2008; Vardoulakis *et al.*, 2002). Fig. 2 shows average indoor CO<sub>2</sub> and BTEX concentrations. This correlation was weaker than that of the NO and BTEX concentrations, as shown in Table 4.

The average indoor concentrations of NO and carbonyls at each home are shown in Fig. 3, and Fig. 4 shows the average indoor CO<sub>2</sub> concentrations and levels of carbonyls. Unlike the BTEX concentrations, levels of carbonyls were more highly correlated with the concentrations of CO<sub>2</sub> than those of NO. The correlation coefficient for carbonyl compounds with CO<sub>2</sub> was 0.61, which was higher than the 0.50 correlation coefficient with NO (see Table 4). The significances of the correlations were summarized in Table S3. Since the CO<sub>2</sub> concentration can serve as an indicator of the ventilation, the high correlation between CO<sub>2</sub> and carbonyl concentrations could indicate that the indoor carbonyl concentration was primarily determined by indoor sources, and

Table 4. Correlation coefficients of BTEX and carbonyls with NO and CO<sub>2</sub>.

	BTEX	Carbonyls
BTEX	1.00	0.78
Carbonyls	0.78	1.00
NO	0.67	0.50
CO <sub>2</sub>	0.59	0.61

reduced with more ventilation.

### 3.3 Correlation of BTEX and Carbonyl Concentrations with House Renovations

Adhesives and paints used for house renovations are known to be strong sources of indoor VOCs (Chen *et al.*, 2014; Maisey *et al.*, 2013; Horemans *et al.*, 2008; Brown, 2002). This study calculated the correlation

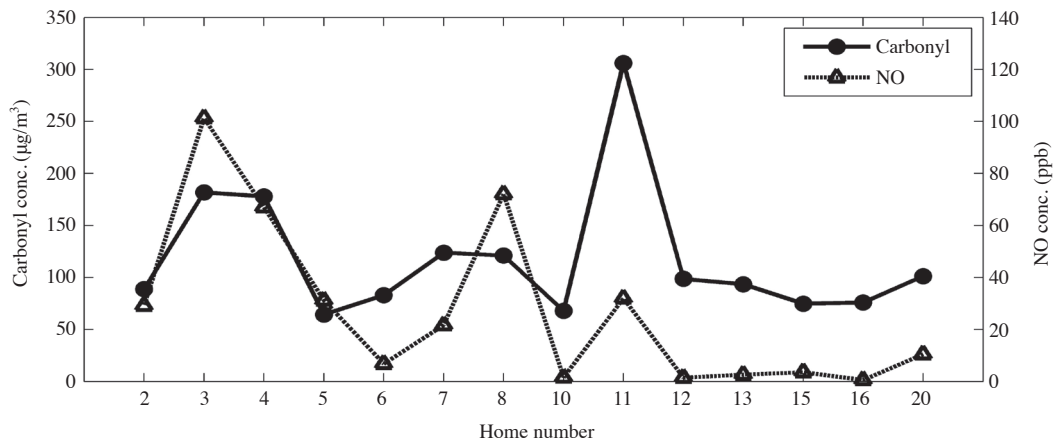


Fig. 3. Average NO and carbonyl concentrations at each home.

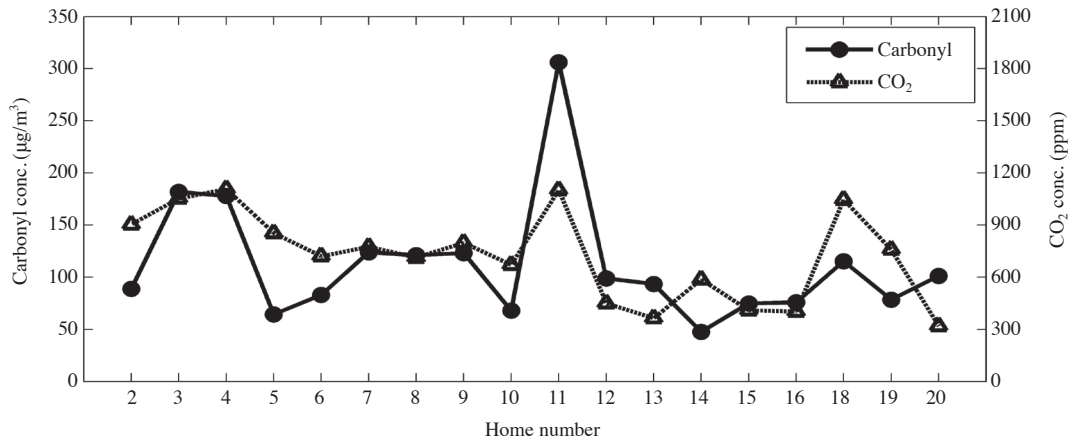


Fig. 4. Average CO<sub>2</sub> and carbonyl concentrations at each home.

Table 5. Correlations between recent house renovations and I/O ratios of BTEX and carbonyls.

	BTEX			Carbonyls		
	Indoor	Outdoor	I/O ratio	Indoor	Outdoor	I/O ratio
Correlation coefficient w/renovation	-0.20	-0.26	0.21	0.00	-0.52	0.64

between house renovations (scored as 1 for renovations within the past two years and 0 for no renovations) and both the concentrations and I/O ratios of BTEX and carbonyls. As seen in Table 5, the I/O ratio of carbonyls showed the strongest correlation with recent renovations. The indoor BTEX concentration was relatively less correlated with renovations, since it was not solely determined by indoor sources, but largely by the outdoor air. Note that the correlation coefficient between outdoor carbonyl concentration and recent house renovations was  $-0.52$ . This is because the renovated

homes were accidentally sampled on days with lower outdoor carbonyl concentrations than those on the non-renovated home sampling days. The significances of the correlations were summarized in Table S3.

However, no significant correlation was found with other possible indoor sources, such as recent furniture purchase, cigarette smoke, or frequencies of dry cleaning and printer usage. This is possibly because the amount of BTEX and carbonyls emitted from those sources are not high enough to determine the overall indoor concentrations of BTEX and carbonyls. On the

**Table 6.** Ratios and correlation coefficients of toluene/benzene and formaldehyde/acetaldehyde.

	Toluene-to-benzene		Formaldehyde-to-acetaldehyde	
	Indoor	Outdoor	Indoor	Outdoor
Average	19.73	14.98	2.60	1.50
Std. dev.	17.40	10.64	0.90	0.44
Correlation coefficient	0.49	0.39	0.52	0.92

**Table 7.** Source apportionment of indoor and outdoor BTEX using PMF.

	Indoor BTEX		Outdoor BTEX	
	Factor1	Factor2	Factor1	Factor2
Benzene	2.44	0.05	2.40	0.01
Toluene	24.02	4.96	12.70	13.97
Ethylbenzene	2.02	4.49	0.31	3.80
Xylenes	1.75	7.23	1.02	3.85
T/B ratio	9.84	99.2	5.29	1397

other hand, a larger number of interior materials were replaced during house renovations, thereby appreciably increasing the indoor levels of BTEX and carbonyls.

### 3.4 Toluene-to-Benzene and Formaldehyde-to-Acetaldehyde Ratios

The toluene-to-benzene ratios for indoors and outdoors were 19.73 and 14.98, respectively (see Table 6). The values obtained in this study were larger than most of those seen in the literature (Buczynska *et al.*, 2009; Horemans *et al.*, 2008; Kerbachi *et al.*, 2006; Zhu *et al.*, 2005; Barletta *et al.*, 2002; Lee *et al.*, 2002; Vardoulakis *et al.*, 2002; Edwards *et al.*, 2001; Hansen and Palmgren, 1996), though one previous study found a ratio of 37, and suggested that this was due to multiple sources of toluene (Ho *et al.*, 2004). Based on the toluene-to-benzene ratio of this study, it is likely that there were multiple sources of BTEX at the sampled homes. This is also confirmed by the correlation coefficients of 0.49 and 0.39, for indoors and outdoors respectively (see Table 6), and the scatter plots in Fig. 5.

The formaldehyde-to-acetaldehyde ratios for indoors and outdoors were 2.60 and 1.50, respectively, which are closer to the values found in the literature (Kume *et al.*, 2008; Moussa *et al.*, 2006; Pang and Mu, 2006; Bakeas *et al.*, 2003; Sin *et al.*, 2001; Christensen *et al.*, 2000; Viskari *et al.*, 2000). In addition, the correlation coefficients between formaldehyde and acetaldehyde were 0.52 and 0.92 for indoors and outdoors, respectively (see Fig. 6 for scatter plots). Our results suggest that carbonyl pollutants arose from a smaller number of sources than did BTEX compounds. The significances of the correlations were summarized in Table S3.

### 3.5 Factor Analysis of Indoor and Outdoor BTEX Using Positive Matrix Factorization (PMF)

Positive matrix factorization (PMF) was performed separately on the indoor and outdoor BTEX concentrations, using EPA PMF 5.0. The two factors, extracted for indoor and outdoor concentrations respectively, are shown in Table 7 along with the calculated toluene-to-benzene ratio (T/B ratio). The PMF result indicates that the concentration profile of BTEX can be explained using two factors, one with a smaller T/B ratio than the average in Table 6 (Factor1), and the other with a very large T/B ratio due to negligible benzene (Factor2). Among previous studies which have reported T/B ratios of traffic related emissions, Ho *et al.* (2004) found an average T/B ratio of 5.2, measured inside a tunnel in Hong Kong. This is similar to the Factor1 T/B ratio from outdoor BTEX, which is 5.29. The higher T/B ratios of other factors are likely to be influenced by various indoor BTEX sources, such as paints and housing materials. The Factor1 from outdoor BTEX may also be influenced by indoor sources, since it was measured at the balconies of high-rise apartments and the front yards of low-rise buildings.

### 3.6 Limitations of This Study

In this study, we measured the concentrations of indoor and outdoor BTEX and carbonyls at 20 homes in Seoul, South Korea from September of 2013 to December of 2014. Since the measurement at each home was conducted at a different day, it is not possible to separately examine the temporal and spatial variations of the concentrations. In Section 3.3, we analyzed the correlation of BTEX and carbonyl concentrations with activi-



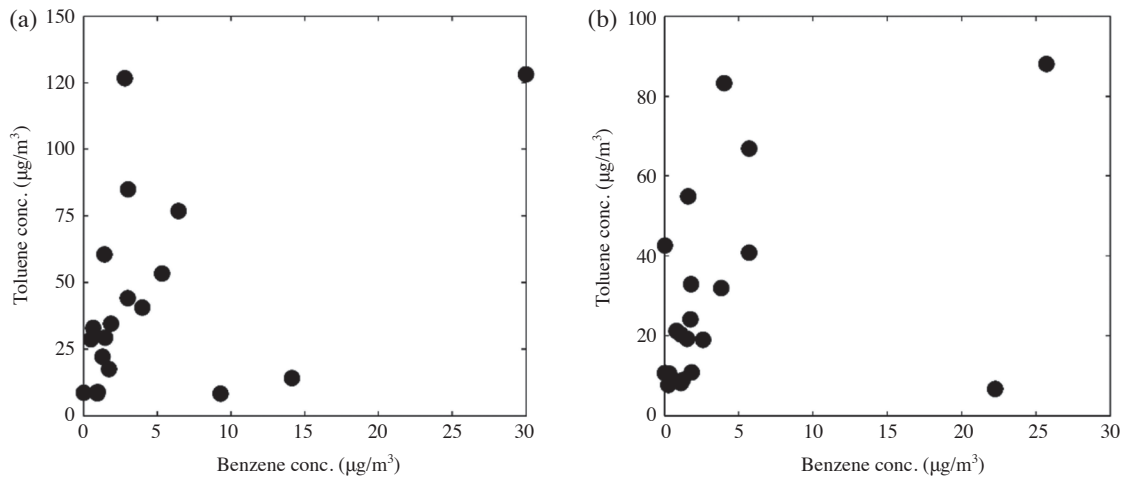


Fig. 5. Scatter plots of (a) indoor and (b) outdoor toluene vs. benzene concentrations.

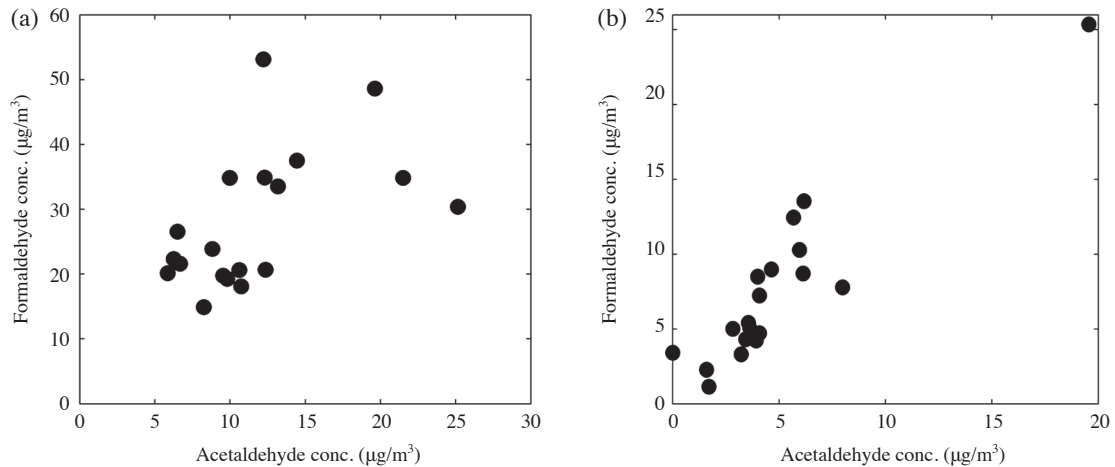


Fig. 6. Scatter plots of (a) indoor and (b) outdoor formaldehyde vs. acetaldehyde concentrations.

ties such as house renovations, the purchase of new furniture, cigarette smoking, dry cleaning, and printing. The information regarding the indoor activity is obtained from a questionnaire distributed to the residents. Therefore, the accuracy of the information may vary from resident to resident, which may result in underestimation of the correlation.

#### 4. CONCLUSIONS

In this paper, indoor and outdoor concentrations of BTEX and carbonyl compounds were measured at 20 homes in Seoul, South Korea. (Carbonyl measurement at one home was eliminated due to sampling error.) The study investigated the characteristics of these compounds by calculating the I/O ratios, toluene-to-benzene

ratios for BTEX, and formaldehyde-to-acetaldehyde ratios for carbonyls; and correlation coefficients of indoor with outdoor concentrations, and of BTEX and carbonyl compounds with the indoor air pollutants NO and CO<sub>2</sub>. The following are the major findings of this work:

- At the homes sampled, the average I/O ratio for BTEX was 1.44, while that for carbonyls was 3.26. The correlation between indoor and outdoor BTEX concentrations was much stronger than between indoor and outdoor carbonyl concentrations (0.91 for BTEX and 0.34 for carbonyls). These results indicate that indoor sources predominantly determined the indoor carbonyl level, whereas both indoor and outdoor sources significantly affected the indoor BTEX level.

- Indoor NO concentrations were highly correlated with levels of BTEX, probably due to both contaminants having originated from traffic emissions.
- Carbonyl concentrations were highly correlated with indoor levels of CO<sub>2</sub>, because both carbonyl and CO<sub>2</sub> originate primarily from indoor sources, and both are easily reduced with increased ventilation.
- A history of interior renovations within the last two years produced the strongest correlation with the I/O ratio of carbonyls.
- The correlation of toluene level with benzene level was lower than that of formaldehyde with acetaldehyde, indicating that there were multiple sources of BTEX and fewer sources of carbonyls at the sampled homes.
- The result of the factor analysis, based on positive matrix factorization, indicated that there are multiple sources of toluene emissions, resulting in higher T/B ratios than those found in previous studies.

This study is important in that it is the first to measure and analyze diverse characteristics of BTEX and carbonyls at homes in Seoul, South Korea. Findings from this study can serve as a guide for further studies to identify the pollution sources. The information on the characteristics and sources of pollutants can be used in implementing plans to reduce and regulate these compounds.

## ACKNOWLEDGEMENT

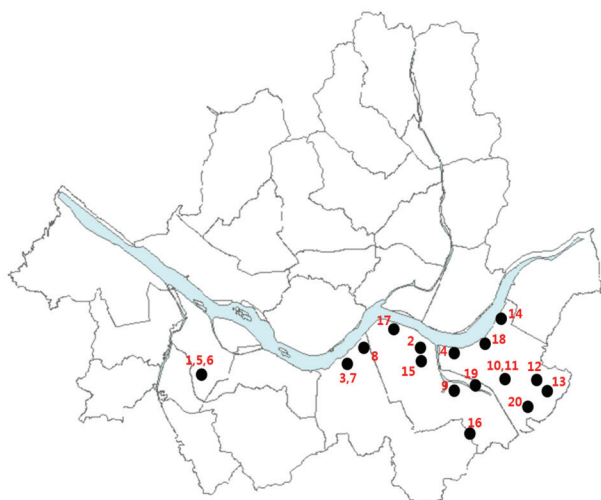
This study was conducted as part of the ANGEL study, which is supported by the Environmental Health Action Program of the Korea Ministry of Environment (Project No. 2013001360004). The authors also thank Kangmo Ahn, M.D., Ph.D.; Youngshin Han, Ph.D.; and Youngmin Kim, Ph.D. from the Environmental Health Center for Atopic Diseases, Samsung Medical Center, Seoul, Korea, for recruiting the sampling homes.

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(Received 14 November 2017, revised 29 January 2018, accepted 7 February 2018)



**Fig. S1.** Geographical information of measurement sites.

**Table S1.** Mean and standard deviations (SD) of field blank samples and limit of detection (LOD) for BTEXS and TVOCs (n = 13).

Compounds	Mean ( $\mu\text{g}/\text{m}^3$ )	SD ( $\sigma$ ) ( $\mu\text{g}/\text{m}^3$ )	LOD (mean + $3\sigma$ ) ( $\mu\text{g}/\text{m}^3$ )
Benzene	2.5	0.6	4.2
Toluene	2.2	1.0	5.2
Ethylbenzene	0.6	0.2	1.1
m-Xylene	2.6	0.5	4.1
Styrene	2.2	0.5	3.7
o-Xylene	2.5	2.3	9.3
TVOC	6.2	3.9	17.9

**Table S2.** Mean and standard deviations (SD) of field blank samples and limit of detection (LOD) for carbonyls (n = 21).

Compounds	Mean ( $\mu\text{g}/\text{m}^3$ )	SD ( $\sigma$ ) ( $\mu\text{g}/\text{m}^3$ )	LOD (mean + $3\sigma$ ) ( $\mu\text{g}/\text{m}^3$ )
Formaldehyde	0.8	0.5	2.3
Acetaldehyde	0.5	0.3	1.5
Acrolein + Acetone	2.0	2.3	9.0
Propionaldehyde	0.8	0.0	0.8
Crotonaldehyde	n.d.	n.d.	n.d.
Methacrolein	n.d.	n.d.	n.d.
2-Butanone	1.0	0.8	3.5
Butyaldehyde	n.d.	n.d.	n.d.
Benzaldehyde	0.2	0.0	0.2
Valeraldehyde	n.d.	n.d.	n.d.
m-Tolualdehyde	0.2	0.0	0.2
Hexaaldehyde	n.d.	n.d.	n.d.
Carbonyls	3.4	3.0	12.3

n.d. indicates "not detected"

**Table S3.** Significance of correlation.

	Correlation coefficient	Number of dataset	p-Value	Confidence interval (95%)
Indoor and outdoor BTEX	0.91	20	2.23e-8	0.79~0.96
Indoor and outdoor carbonyls	0.34	19	0.150	-0.13~0.69
Indoor BTEX and indoor carbonyls	0.78	19	0.001	0.51~0.91
Indoor BTEX and indoor NO	0.67	14	0.0092	0.21~0.88
Indoor BTEX and indoor CO <sub>2</sub>	0.59	19	0.0081	0.18~0.82
Indoor carbonyls and indoor NO	0.50	14	0.071	-0.05~0.81
Indoor carbonyls and indoor CO <sub>2</sub>	0.61	18	0.0075	0.20~0.84
Indoor BTEX and renovation	-0.20	16	0.46	-0.63~0.33
Outdoor BTEX and renovation	-0.26	16	0.34	-0.67~0.27
I/O ratio of BTEX and renovation	0.21	16	0.44	-0.32~0.64
Indoor carbonyls and renovation	0.00	15	0.99	-0.51~0.51
Outdoor carbonyls and renovation	-0.52	15	0.045	-0.82~-0.02
I/O ratio of carbonyls and renovation	0.64	15	0.010	0.19~0.87
Indoor toluene and indoor benzene	0.49	20	0.030	0.06~0.76
Outdoor toluene and outdoor benzene	0.39	20	0.089	-0.06~0.71
Indoor formaldehyde and indoor acetaldehyde	0.52	19	0.022	0.09~0.79
Outdoor formaldehyde and outdoor acetaldehyde	0.92	19	0.0000	0.80~0.97