



Spatial and temporal variations of volatile organic compounds using passive air samplers in the multi-industrial city of Ulsan, Korea

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Abstract

The source-receptor relationship of volatile organic compounds (VOCs) is an important environmental concern, particularly in large industrial cities; however, only a few studies have identified VOC sources using high spatial resolution data. In this study, 28 VOCs were monitored in Ulsan, the biggest multi-industrial city in Korea. Passive air samplers were seasonally deployed at eight urban and six industrial sites. The target compounds were detected at all sites. No significant seasonal variations of VOCs were observed probably due to the continuous emissions from major industrial facilities. Benzene, toluene, ethylbenzene, xylenes, and styrene accounted for 66–86% of the concentration of Σ_{28} VOCs. The spatial distribution of the individual VOCs clearly indicated that petrochemical, automobile, non-ferrous, and shipbuilding industries were major VOC sources. Seasonal wind patterns were found to play a role in the spatial distribution of VOCs. Diagnostic ratios also confirmed that the industrial complexes were the dominant VOC sources. The results of principal component analysis and correlation analyses identified the influence of specific compounds from each industrial complex on individual sites. To the best of our knowledge, this is the first comprehensive report on the seasonal distribution of VOCs with high spatial resolution in a metropolitan industrial city in Korea.

Keywords VOCs · Passive air sampler · Spatial distribution · Source identification

Introduction

Volatile organic compounds (VOCs), a major type of hazardous air pollutants (HAPs), significantly affect air quality, and they can have an adverse effect on human health (Jo et al. 2012; Valach et al. 2014). VOCs are emitted from both natural sources such as shrubs and grasslands and anthropogenic sources such as industrial activities and vehicle emissions (Bhattacharya et al. 2015; Tassi et al. 2013). VOCs react with nitrogen oxides (NO_x) in the presence of sunlight, then ozone

(O_3) and secondary organic aerosols (SOA) are produced (Sarkar et al. 2014; Warneke et al. 2014). They can adversely affect crop yield, air quality, and human health (Pugliese et al. 2014; Villanueva et al. 2014), causing complications such as asthma, allergies, headaches, and chronic obstructive pulmonary diseases (Chen et al. 2015, 2016; Saalberg and Wolff 2016). On account of these possible severe health effects, some carcinogenic compounds (e.g., 1,3-butadiene, benzene, and vinyl chloride) (IARC 2016) have been listed in the US-EPA HAPs list (US-EPA 1999).

Passive air samplers, which collect VOCs through molecular diffusion onto activated charcoal in an adsorption cartridge, are generally used to monitor both indoor and outdoor VOCs (Demirel et al. 2014; Geiss et al. 2011; Tovalin-Ahumada and Whitehead 2007). Performance evaluations (Pennequin-Cardinal et al. 2005) and comparisons of samplers (Lan and Binh 2012) have also been conducted. Passive air samplers provide relatively high spatial resolution data of VOCs because they are cost-effective and easy to operate without electricity (Bruno et al. 2008; Gallego et al. 2011). Seasonal monitoring studies using passive air samplers were conducted on 58 VOCs at 40 industrial sites in Aliaga, Turkey

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(Dumanoglu et al. 2014), on benzene, toluene, ethylbenzene, and xylenes (BTEX) at 50 industrial sites in Windsor, Canada (Miller et al. 2012), and on BTEX at four urban sites in Delhi, India (Hoque et al. 2008); however, the results of these studies did not fully reflect the seasonal VOC variations because the samplers were only used for short periods of only 1 or 2 weeks in each of the four seasons or were deployed for only one or two seasons (Bruno et al. 2008; Kerchich and Kerbachi 2013; Miller et al. 2009; Roukos et al. 2009; Terrés et al. 2010).

A variety of methods have been applied to source identification of VOCs. For example, diagnostic ratios are frequently used to characterize traffic emission, photochemical age, and long-range transport (Miller et al. 2012; Tiwari et al. 2010). A simple statistical approach, such as correlation analysis, can provide information on potential sources of VOCs (Hoque et al. 2008; Miller et al. 2009). In addition, multivariate statistics can be used; principle component analysis (PCA) extracts several factors related to the main sources of target compounds (An et al. 2014; Hsieh et al. 2006). Furthermore, positive matrix factorization (PMF) can be applied to identify VOC sources and quantify their contributions (Civan et al. 2015; Dumanoglu et al. 2014; Zhang et al. 2014).

According to the Pollutant Release and Transfer Registers (PRTR) system in Korea (MOE 2014e), the metropolitan city of Ulsan had the highest emission density (7.7 t/km^2) in Korea, emitting 8139 t of toxic chemicals annually. Ulsan is basically an industrial city that has many large-scale industrial complexes (e.g., petrochemical, automobile, non-ferrous, and shipbuilding industries), all of which have been found to be major VOC emission sources. Recent studies on ambient air pollution in Ulsan have focused on polycyclic aromatic hydrocarbons (PAHs) (Choi et al. 2012) and criteria air pollutants (CAPs) (Clarke et al. 2014), such as ozone (Lee et al. 2007; Susaya et al. 2013) and particulate matter (PM) (Lee et al. 2004); however, very few VOC studies have been conducted using active air samplers at several sites (Na et al. 2001; Shin and Jo 2012). Although there are two national HAPs monitoring network stations in Ulsan, it has been difficult to determine the spatial distribution of VOCs. Therefore, the source-receptor relationship of VOCs in Ulsan based on their spatial distributions has not been fully investigated yet.

In this study, passive air sampling of VOCs was seasonally conducted at 14 sites in Ulsan, Korea. The objectives of this study were (1) to investigate the levels and patterns of VOCs, (2) to determine spatial and temporal distributions of VOCs, and (3) to identify the main sources of VOCs. To the best of our knowledge, this is one of the most comprehensive VOC monitoring studies conducted in industrial cities in Korea and the first to conduct VOC monitoring using passive air samplers in Ulsan.

Materials and methods

Passive air sampling

The study area (1061 km^2) is located in the southeastern part of South Korea along the East Sea (Fig. 1). Passive air samplers were deployed at 14 sites, which were classified into eight urban (U1–U8) and six industrial (I1–I6) sites (Fig. S1 in the Supplementary Information). Among the 14 sites, 11 sites were part of the urban air monitoring network operated by the Ulsan Institute of Health and Environment (UIHE). Three further sites were selected from two industrial areas (I5 and I6) and one urban area (U2) to increase the spatial resolution of the VOC data. The three sites were classified by their distance from industrial complexes and population.

The passive air samplers (Radiello™ diffusive sampling system) were purchased from SIGMA-ALDRICH (<https://www.sigmaaldrich.com>). It has a diffusive body, a supporting plate, and an adsorption cartridge made up of a stainless steel net cylinder with a 100 mesh-grid opening of 5.8 mm diameter. The net cylinder was packed with 530 mg of activated charcoal with a particle size of 35–50 mesh (Fig. S2). The samplers were deployed over four seasons, with two monitoring periods: summer (July 2–31 and July 31–August 29, 2014), fall (October 8–November 7 and November 7–December 5, 2014), winter (January 8–February 3 and February 3–March 3, 2015), and spring (April 10–May 8 and May 8–June 7, 2015). Back diffusion is likely to occur for long sampling time, but the sampling time in this study was about 30 days, which is within the range of sampling time (15 min to 30 days) using the Radiello™ diffusive sampling system. In addition, back diffusion was not considered based on the reference sampling volume of 3050 L at $10 \mu\text{g}/\text{m}^3$ of benzene before back diffusion occurred. Duplicate samples were collected from all sampling sites in spring 2015 and from four industrial sites in the other seasons. As samples at one industrial site (I5) were lost during the first spring 2015 monitoring period, a total of 162 samples were collected for assessment. After the sampling was completed, all cartridges were stored in glass containers at $-4 \text{ }^\circ\text{C}$ until analysis.

Analysis and QA/QC

There were 28 compounds targeted in this study: benzene, ethylbenzene, m,p-xylenes, o-xylene, styrene, toluene, 1,1,1-trichloroethane, 1,1,2-trichloroethane, 1,1-dichloroethylene, 1,2,4-trichlorobenzene, 1,2-dichlorobenzene, 1,2-dichloroethane, 1,2-dichloropropane, 1,4-dichlorobenzene, bromodichloromethane, bromoform, carbon tetrachloride, chlorobenzene, chloroform, cis-1,2-dichloroethylene, dibromochloromethane, dichloromethane, tetrachloroethylene, trans-1,2-dichloroethylene, trichloroethylene, vinyl chloride, 1,3-butadiene, and methyl tert-butyl ether (MTBE). These

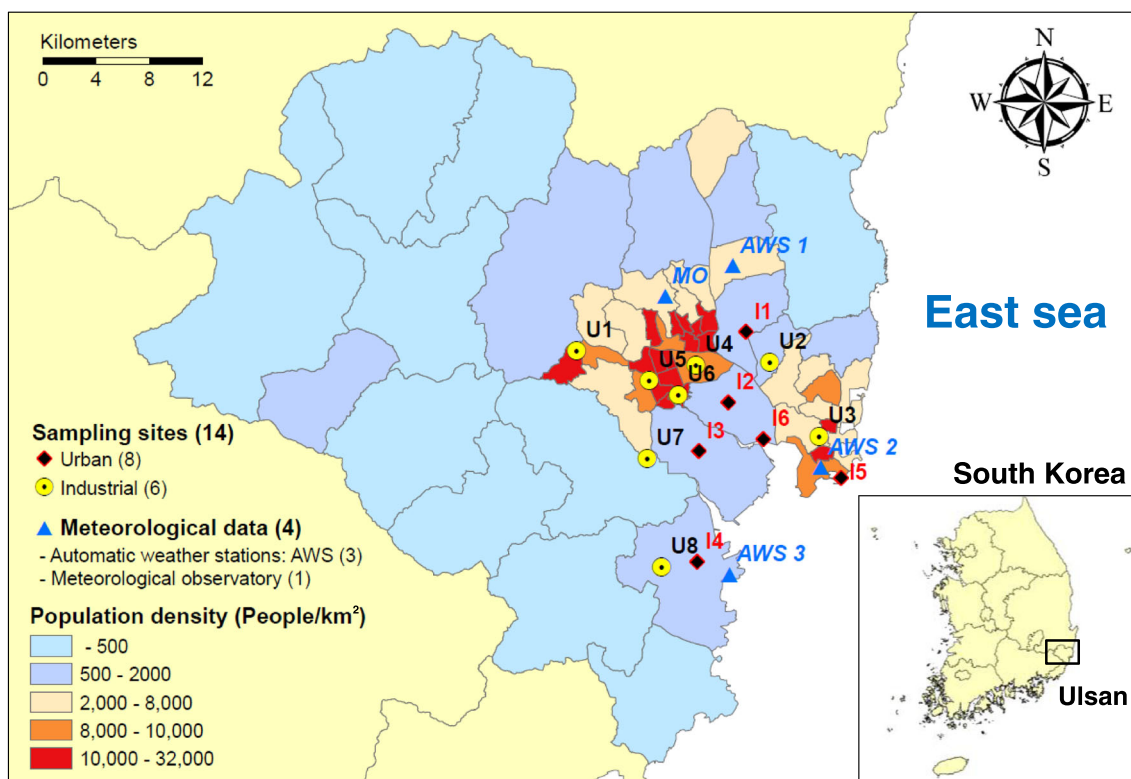


Fig. 1 Locations of the 14 sampling sites, three automatic weather stations, and a meteorological observatory on a population density map for Ulsan, Korea. The map was drawn using ArcGIS 10.4.1 (ESRI Inc., USA)

compounds are classified into aromatic, halogenated, and alkane and oxygenated groups. Detailed information on the target compounds is shown in Table S1 in the Supplementary Information.

After sampling, the target compounds were extracted from the cartridges using 2 mL of carbon disulfide (CS₂). As surrogate standards, deuterated compounds (methylene chloride-d₂, 1,2-dichloroethane-d₄, benzene-d₆, toluene-d₈, chlorobenzene-d₅, ethylbenzene-d₁₀, 1,2-dichlorobenzene-d₄, and 1,4-dichlorobenzene-d₄) were inserted into the cartridges before extraction, after which the samples were extracted for 30 min using an ultrasonic bath, and a 1 mL extract was transferred to a vial. Before the analyses, fluorobenzene was added to the vial as an internal standard.

After the pretreatment procedure, the samples were analyzed using a gas chromatograph/mass spectrometer (GC/MS, Agilent 7890N/5975C). A DB-624 column (60 m × 0.25 mm i.d. and 1.4 μm film thickness) was used to separate the target compounds, and a helium carrier gas with a flow rate of 1.0 mL/min was employed. Of the final sample, 1 μL was injected into the GC in split mode (25:1 and 30 mL/min), and selective ion monitoring (SIM) mode was applied. The oven temperatures were as follows, 40 °C for the initial 3 min, which was then increased at 8 °C/min up to 90 °C and maintained for 4 min, and then increased at 6 °C/min up to 200 °C and maintained for 5 min. The ions were observed in electron ionization (EI) mode.

Field blanks were taken ($n = 24$ for the whole monitoring periods), and data were blank corrected. The average sample recovery ranged from 40 to 70%. The method detection limits (MDLs) were calculated using the following equation.

$$MDL = t_s \times SD \tag{1}$$

where t_s is the Student's t value at 99% confidence, and SD is the standard deviation for each target chemical's concentration in spiked samples ($n = 7$, spiked amount 0.1 μg). The MDL samples were analyzed using the same analytical procedure as for the real samples. The MDLs were in a range of 0.017–0.200 μg/m³. The mean coefficient of variation (CV) for total VOCs between the duplicated samples was $8.2 \pm 4.0\%$.

Calculation of VOC concentrations

Time-averaged concentrations (C) were calculated using Eq. 2 (Maugeri-IRCCS 2006).

$$C (\mu\text{g}/\text{m}^3) = \frac{M (\mu\text{g})}{Q_k (\text{mL}/\text{min}) \times t (\text{min})} \times 10^6 \tag{2}$$

where M is the mass of chemical adsorbed by the cartridges (μg), t is the sampling period (min), and Q_k is the chemical-specific sampling rate calculated using Eq. 3.

$$Q_k = Q_{298} \left(\frac{K}{298} \right)^{1.5} \times 10^6 \quad (3)$$

where Q_{298} is the sampling rate in the normal condition (298 K) provided by the manufacturer (Maugeri-IRCCS 2006), and K is the absolute temperature during the sampling period.

Statistical analysis

A rank sum test using SigmaPlot 12.0 (Systat Inc., USA) was conducted to examine the statistical differences between the groups. Correlation and principal component analyses (PCA) using a VARIMAX rotation were performed using IBM SPSS statistics 20.0 (IBM, USA) for source identification. The input data from each season were slightly different because several VOCs that had less than a 50% detection were excluded. For the PCA, the top 10 VOCs with the highest concentrations for the individual seasons were selected as input data, which were normalized using the sum of the ten selected compounds for each sample.

Results and discussion

Seasonal variations of total VOCs

The concentrations of total VOCs were in a range of 7.8–62.0 $\mu\text{g}/\text{m}^3$ (mean 23.6 $\mu\text{g}/\text{m}^3$, median 18.2 $\mu\text{g}/\text{m}^3$) in summer, 12.7–54.8 $\mu\text{g}/\text{m}^3$ (mean 28.1 $\mu\text{g}/\text{m}^3$, median 25.9 $\mu\text{g}/\text{m}^3$) in fall, 11.0–40.0 $\mu\text{g}/\text{m}^3$ (mean 19.6 $\mu\text{g}/\text{m}^3$, median 16.8 $\mu\text{g}/\text{m}^3$) in winter, and 11.2–67.0 $\mu\text{g}/\text{m}^3$ (mean 32.3 $\mu\text{g}/\text{m}^3$, median 29.5 $\mu\text{g}/\text{m}^3$) in spring (Fig. 2). The average concentration of total VOCs was the highest in spring, followed by fall, summer, and winter. Statistical differences were found between spring and summer, spring and winter, and fall and winter (rank sum

test, $p < 0.05$). The same seasonal patterns of total VOCs were observed for the industrial and residential sites.

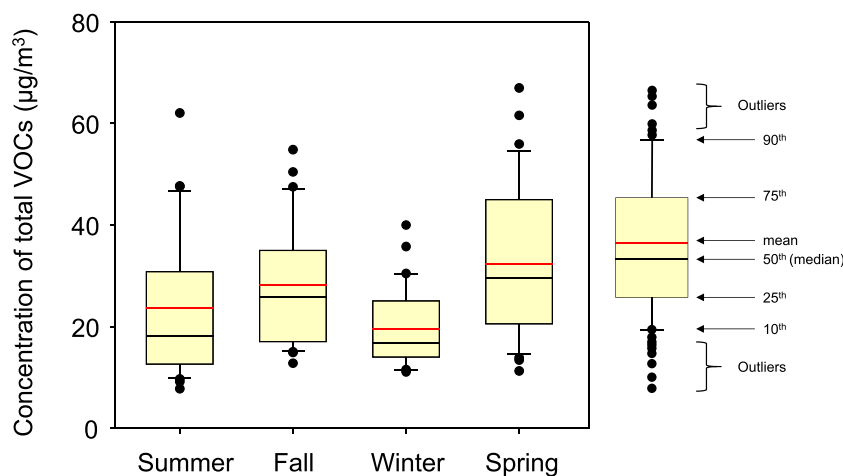
The concentrations of VOCs can increase in the warmer seasons because of the enhanced volatilization from the surface environment, and elevated levels of VOCs in the cold seasons can occur in stable atmospheric conditions (i.e., limited dilution). For these reasons, previous studies have reported different seasonal patterns of VOC levels: spring>summer>winter>fall in rural areas in Luding, China (Zhang et al. 2014), fall>spring>summer>winter in industrial areas in Aliaga, Turkey (Dumanoglu et al. 2014), summer>spring>fall>winter in industrial areas in Nanjing, China (An et al. 2014), and winter>spring>fall>summer in urban areas in Rome, Italy (Fanizza et al. 2014). Consequently, it is difficult to generalize a seasonal trend of VOCs from former studies.

Even though the concentrations of total VOCs in Ulsan were seasonally different, the concentrations in spring were only 1.6 times higher than those measured in winter. This result indicates that the seasonal variations of VOCs in Ulsan were not severe, possibly because of the relatively constant emissions from industrial facilities throughout the year and meteorological conditions (Table S2). For example, evaporation of VOCs can be enhanced in the summer by increased temperature, but more precipitation also results in a decrease in VOC concentrations. The influence of seasonal wind patterns will be discussed in the section “Spatial distribution of VOCs”. Also, the HAPs monitoring network of Korea indicated weak seasonal variations of VOCs in Ulsan (MOE, 2014a, b, c, d, 2015a, b, c, d).

Levels of individual VOCs

The annual mean concentrations for each compound are shown in Fig. 3, and the seasonal mean concentrations for each compound are shown in Fig. S3. The aromatic group was found to have the highest mean concentration (20.1 $\mu\text{g}/\text{m}^3$), followed by the halogenated (5.9 $\mu\text{g}/\text{m}^3$) and the alkane

Fig. 2 Box plots for the total concentrations for the 28 target compounds (Σ_{28} VOCs) at 14 sites in Ulsan, Korea over four seasons (July 2014–June 2015)



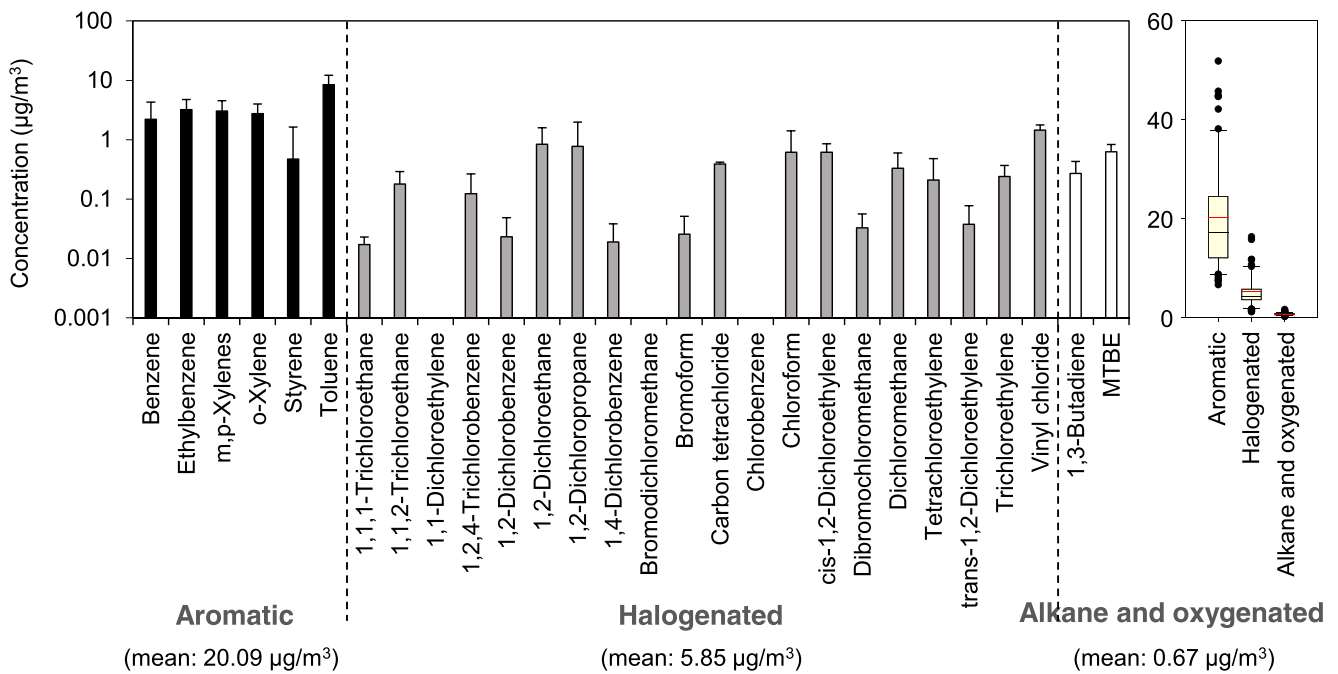


Fig. 3 Annual (July 2014–June 2015) mean concentrations for 28 target compounds at 14 sites in Ulsan, Korea. The error bars represent the standard deviations. A box plot is presented to summarize the distributions of the target chemicals in three VOC groups

and oxygenated groups (0.7 µg/m³). The aromatic group accounted for 75% of the annual concentration of total VOCs. Toluene was found to have the highest mean concentration (8.4 µg/m³), followed by ethylbenzene (3.2 µg/m³), m,p-xylenes (3.0 µg/m³), o-xylene (2.7 µg/m³), and benzene (2.2 µg/m³) (Fig. 3). Three compounds (1,1-dichloroethylene, bromodichloromethane, and chlorobenzene) were not detected in the 28 target compounds. The seasonal patterns for the target compounds were generally similar (Fig. S3).

The concentrations of BTEX in this study were compared with data from previous studies (Table 1). Toluene is also a dominant compound in the previous studies. The results in this study (19.6 µg/m³ of Σ BTEX) were similar to or higher than the results from other countries except for Italy (41.9 µg/m³) (Bruno et al. 2008), which was directly influenced by vehicular emissions. In contrast, a clear difference was found between Ulsan and Seoul in Korea, with the Σ BTEX concentrations in this study being two times higher in Ulsan than in Seoul (9.9 µg/m³) (Kim et al. 2012); however, the levels of toluene in both cities were similar because of common toluene sources (e.g., vehicle fuels, paints, paint thinners, rubbers, and adhesives) in the urban and industrial areas. In Ulsan, the concentrations (40.5 µg/m³) in 1997 (Na et al. 2001) were reported to be much higher than those in Seoul and the results from this study, which could suggest that BTEX emissions in Ulsan had decreased substantially by enforced governmental regulations through the Clean Air Conservation Act. Since 1996, the emissions of VOCs from industrial facilities have been regulated by this act; however, recent data from the HAPs monitoring network (MOE, 2014a, b, c, d, 2015a, b,

c, d) showed no apparent VOC decreases at the two sites (urban: Sinjeong (U4), industrial: Yecheon (I2)) in Ulsan after the mid-2000s, which may have been because of the larger population, the greater number of registered vehicles, and petrochemical products.

The HAPs monitoring network data (13 compounds) in Ulsan over the same period (July 2014–June 2015) were compared with our data (Fig. S4), from which it was found that the VOC concentrations (especially BTEX) in this study were higher than those measured at the urban site. An opposite result, particularly for m,p-xylenes, was observed at the industrial site in fall 2014. These differences could be explained from the time-averaged concentrations derived for this study, whereas 13 VOCs were measured for 1 day (24 h) per month using active air samplers in the HAPs monitoring network. Nonetheless, the overall levels and patterns for the 13 VOCs in the two studies were comparable.

Spatial distribution of VOCs

The annual and seasonal mean concentrations of total VOCs and BTEX at each sampling site are shown in Fig. S5. As expected, the industrial sites showed higher levels of VOCs than the urban sites; the annual concentrations of total VOCs and BTEX were 34.5 µg/m³ and 24.9 µg/m³ at the industrial sites and 20.7 µg/m³ and 15.7 µg/m³ at the urban sites, respectively. Similar spatial distributions were observed during all seasons except for Sites I2 and U2. Although Site I2 is close to a petrochemical industrial complex, the VOC concentrations were lower than those at other industrial sites and

Table 1 Comparisons of the mean concentrations ($\mu\text{g}/\text{m}^3$) for benzene, toluene, ethylbenzene, m,p-xylenes, and o-xylene (BTEX) in selected countries

Country	City	Site	Period	Sampler	Benzene	Toluene	Ethylbenzene	m,p-Xylenes	o-Xylene	Σ BTEX	Reference
Algeria	Algiers	Urban and semirural	Mar–May 2009	PAS	2.5	6.6	2.5	6.1	3.1	20.8	Kerchich and Kerbachi (2013)
Canada	Windsor	Urban and industrial	Four seasons 2004–2006	PAS	0.8	2.8	0.5	1.4	0.5	6.0	Miller et al. (2012)
France	Dunkerque	Urban and industrial	Jan and Jun 2007	PAS	1.2	3.0	1.3	1.1	0.6	7.1	Roukos et al. (2009)
Italy	Canosa di Puglia	Urban	Oct and Nov 2006	PAS	4.7	15.6	3.5	15.3	2.8	41.9	Bruno et al. (2008)
Turkey	Izmir	Industrial	Four seasons 2009–2010	PAS	2.7	7.7	0.6	2.8	0.7	14.5	Dumanoglu et al. (2014)
Korea (1997)	Ulsan	Urban and industrial	Jun 1997	AAS	5.3	14.6	3.5	12.8	4.3	40.5	Na et al. (2001)
Korea (2009)	Seoul	Urban	Feb–Dec 2009	AAS	0.6	7.6	0.6	0.8	0.3	9.9	Kim et al. (2012)
Korea (2014)	Ulsan	Urban and industrial	Four seasons 2014–2015	PAS	2.2	8.4	3.2	3.0	2.7	19.6	This study

PAS passive air sampler, AAS active air sampler

similar to the concentrations at the urban sites possibly due to the predominant wind directions (northwesterly). On the contrary, high VOC concentrations similar to those at the industrial sites were found at an urban site (U2), possibly because of a nearby automobile industrial complex with painting, adhesion, cleaning, and coating processes.

The spatial distributions of VOCs were also examined using a geographic information system (ArcGIS 10.4.1, ESRI Inc., USA). As an interpolation method, inverse distance weighting (IDW) was employed. Contour plots of seasonal distributions of total VOCs and wind roses at the Ulsan meteorological observatory (MO) are presented in Fig. 4, and the annual distributions of total VOCs are shown in Fig. S6. The annual levels of total VOCs at all industrial sites and one urban site (U2) were higher than at the other urban sites, indicating that the four major industrial complexes (petrochemical, automobile, non-ferrous, and shipbuilding industries) are the primary sources of VOCs. This result was also supported by similar spatial distributions of the annually measured BTEX and the PRTR emission data, as shown in Fig. S7. More specifically, the levels of benzene were relatively high at Site I6 in the petrochemical industrial complex and at Site I4 in the non-ferrous industrial complex, and these areas also had larger benzene emissions. Meanwhile, the emission data from the petrochemical industrial complex did not strongly match the measured data because benzene emissions may have mixed sources including vehicle exhaust. For toluene, both the measured data and the emission data showed higher levels at the automobile industrial complex. The ethylbenzene and xylene concentrations were higher in the automobile, shipbuilding, and petrochemical industrial complexes. These measured data were also supported by the emission data.

Sites U2 and I6 were found to be hot spots of VOC pollution in summer (Fig. 4a), probably because the toluene-emitting automobile industrial facilities are densely distributed around Site U2 (also I1) (Fig. S7). The BTEX measured data and emission data were found to have similar spatial distributions; however, Site I6 has a benzene concentration ($15.06 \mu\text{g}/\text{m}^3$) three times higher than the annual European Union limit of $5 \mu\text{g}/\text{m}^3$ because of the strong influence of the petrochemical processes as well as vehicle exhaust, which was also suspected to be a major benzene source (Miller et al. 2012). This result is discussed further in the next section of source identification. The concentrations of total VOCs in spring (Fig. 4d) were higher than in summer at all sampling sites except I6, with the similar spatial distributions in both seasons because of the prevailing easterly and westerly winds. In fall and winter, the northwesterly winds were speculated to bring large amounts of VOCs emitted from the industrial complexes to the East Sea. As northeasterly winds were also observed in fall (Fig. 4b), this wind pattern appeared to be the reason for the elevated ethylbenzene and xylene

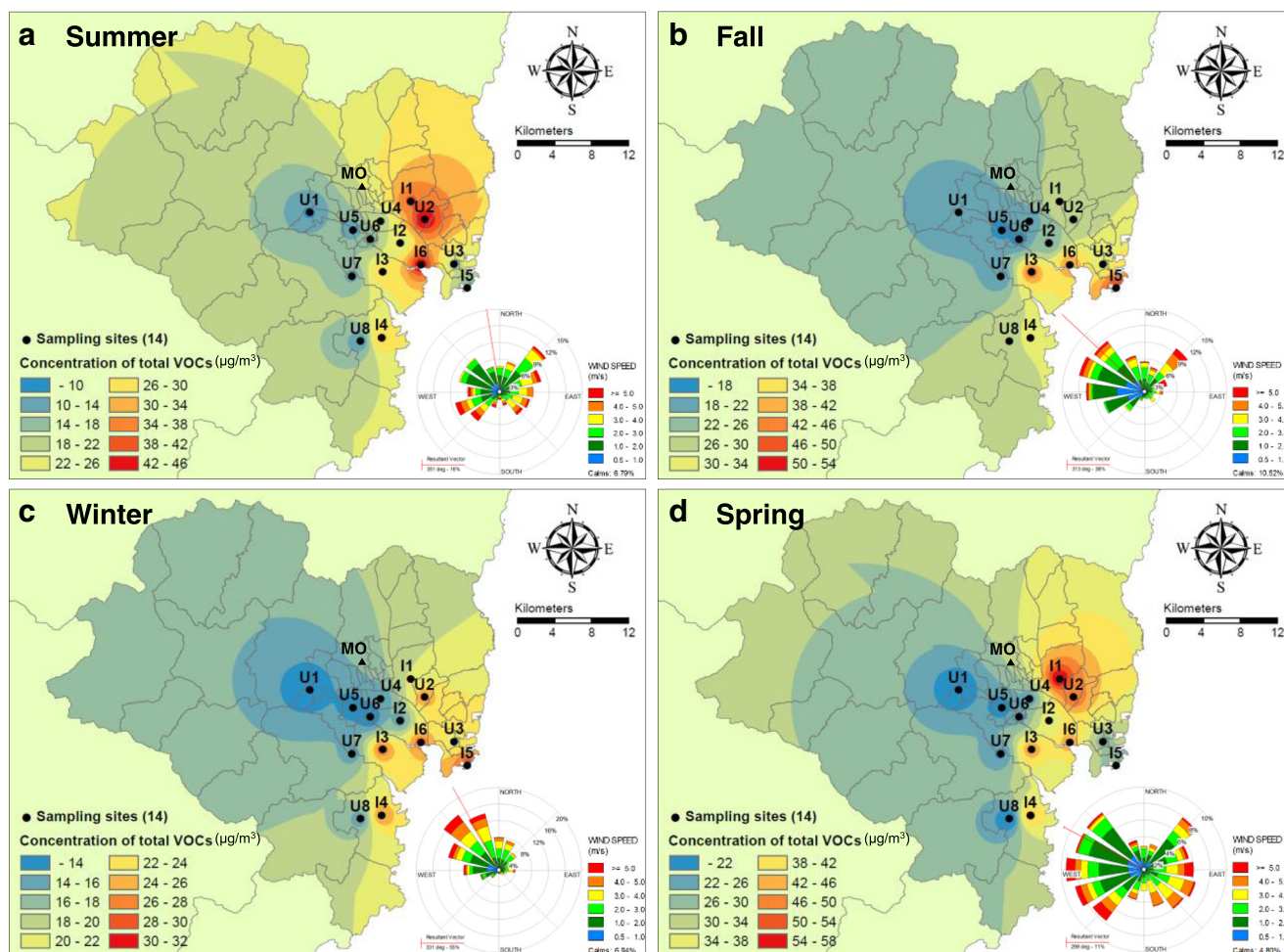


Fig. 4 Seasonal spatial distributions of total VOC concentrations and predominant wind directions in Ulsan, Korea

concentrations at Site I5, with the major ethylbenzene and xylene sources located in a northeast direction from Site I5 (Fig. S7). These results indicate that wind patterns played an important role in the spatial distributions of VOCs. More discussion on the distributions of the other minor compounds can be found in Text S1 in the Supplementary Information.

Source identification of VOCs

The monitoring data can be used to identify the major air pollutant sources using various diagnostic ratios and statistical analyses (e.g., PCA and correlation analysis). Toluene/benzene (T/B) and m,p-xylenes/ethylbenzene (X/E) ratios have been widely used to obtain preliminary source information. The T/B ratio can be used to evaluate the influence of traffic and non-traffic sources (Shi et al. 2015). Both benzene and toluene are emitted from vehicles, but benzene is a well-known marker of the vehicular exhaust (Miller et al. 2012), and toluene is mainly evaporated from paint solvents (Liu et al. 2008). Several previous studies have reported that ratios lower than 1 (Tiwari et al. 2010), 2 (Yurdakul et al. 2013), 3

(Jaars et al. 2014), 4.3 (Miller et al. 2012) or in a range of 1.5–3.0 (Miller et al. 2011) indicate a high traffic source contribution, and higher ratios indicate non-traffic sources (e.g., solvent evaporation); a much higher T/B ratio could also indicate the effect of industrial facilities (Ho et al. 2004). Based on these previous studies, in this study, a T/B ratio of three was used to distinguish the traffic (<3.0) and non-traffic effects (>3.0).

The T/B ratios for all data are shown in Fig. 5a. The ratios were in ranges of 0.8–23.4 (mean 6.9) in summer, 1.7–12.9 (mean 7.0) in fall, 1.2–6.9 (mean 3.9) in winter, and 1.0–18.3 (mean 5.9) in spring, with the non-traffic effects being more dominant in all seasons. Much higher T/B ratios were observed at two urban sites (U2 and U3) close to automobile and ship-building industrial complexes, indicating that these industries were a primary toluene source. Meanwhile, much lower T/B ratios were found at Sites I3, I4, and I6. As Sites I3 and I4 were respectively next to roads in the petrochemical and non-ferrous industrial complexes, there would be higher benzene concentrations from both the traffic and the industrial effects. Site I6, which was also near the petrochemical industrial complex, was possibly more influenced by traffic emissions in spring and

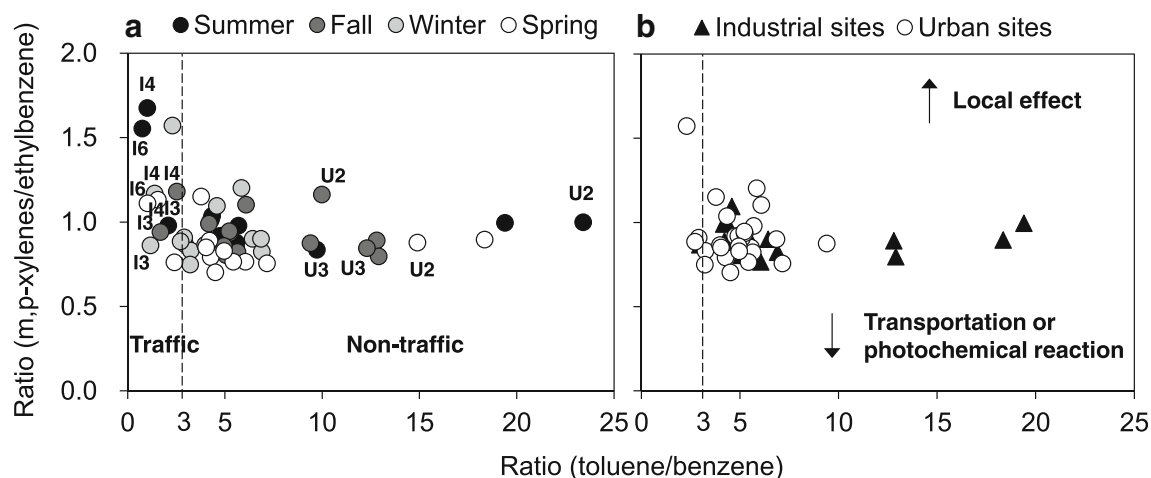


Fig. 5 Diagnostic ratios of toluene/benzene (T/B) and m,p-xylenes/ethylbenzene (X/E) by (a) season and (b) land use (U2, U3, I3, I4, and I6 were excluded) at all sampling sites

summer due to the whale museum, one of the most famous tourist attractions in Ulsan; Korean tourism statistics (<http://www.tour.go.kr/>) reported that 5.4 times more tourists visit the museum for whale watching cruises in summer and spring (18,666 people) than in fall and winter (3459 people). In Fig. 5b, data from Sites U2, U3, I3, I4, and I6 were excluded to better understand the differences between the industrial and urban sites, from which it can be seen that the ratios at several of the industrial sites were significantly higher than those at the urban sites. The T/B ratios in winter were generally lower than those in the other seasons. This observation can be explained by the seasonal variation of fuel formulations, which is more volatile in winter (Miller et al. 2012), and more evaporation of gasoline with a high content of toluene in summer (Ho et al. 2004). Furthermore, the major northwesterly winds (Fig. 4c) in the winter could reduce the influence of toluene emissions from the industrial complexes.

The X/E ratio indicates the aging of VOCs in the atmosphere; that is, it can diagnose the effects of local pollution, transport, or photochemical reactions (Nelson and Quigley 1983). The atmospheric lifetimes of benzene and toluene are 12.5 and 2.0 days, respectively (Liu et al. 2008), which are rather stable, while those of m,p-xylenes and ethylbenzene are 3 and 8 h, respectively (Shi et al. 2015). As m,p-xylenes react more rapidly than other compounds, a lower X/E ratio indicates the aging of VOCs in the atmosphere. The X/E ratios in this study were in ranges of 0.8–1.7 (mean 1.0) in summer, 0.8–1.2 (mean 0.9) in fall, 0.7–1.6 (mean 1.0) in winter, and 0.7–1.2 (mean 0.9) in spring; therefore, there were no significant differences in X/E ratios between the seasons and the sites. This result suggests that they are emitted continually from the industrial facilities regardless of the season. In previous studies, X/E ratios were 2.6–3.7 (mean 3.0) at urban sites in Canada (Miller et al. 2012), 1.1–3.0 (mean 2.0) at industrial sites in China (Shi et al. 2015), and 0.4–0.7 (mean 0.5) at urban and industrial sites in Taiwan (Liu et al. 2008).

The ratios in this study were a little lower or similar to those reported in other studies.

The results of the PCA for spring are shown in Fig. 6, and the results for the other seasons are shown in Fig. S8. The PCA results for the different seasons were similar. In the spring data, three components (X-axis: PC1, Y-axis: PC2, and Z-axis: PC3) with Eigenvalues over 1 were selected, which respectively accounted for 37%, 21%, and 15% of the total variances. Three groups were classified in the score plot (Fig. 6a): Group 1 (U2, U3, I1, and I5), Group 2 (urban sites), and Group 3 (I2, I4, and I6). The loading plot (Fig. 6b) shows that toluene, o-xylene, ethylbenzene, and m,p-xylenes were more influential in Group 1. Actually, Sites I1 and U2 are located in the automobile industrial complex, which mainly emits toluene (Fig. S7b). Meanwhile, Sites I5 and U3 were contaminated mainly with xylenes and ethylbenzene from the shipbuilding industrial complex, and Group 3 had higher contributions of cis-1,2-dichloroethylene, benzene, and chloroform. As discussed, relatively high benzene concentrations were detected at Sites I4 and I6. The urban sites in Group 2 were possibly influenced by the various sources of Groups 1 and 3 and Site I3 (petrochemical facilities). The urban sites were also characterized by vinyl chloride, carbon tetrachloride, and MTBE (Figs. 6 and S8). As Site I2 is at the edge of the petrochemical industrial complex and close to the urban sites, this site had similar characteristics to the urban sites. Site I3, characterized by 1,2-dichloropropane, was found to vary significantly from the three groups in all seasons. 1,2-dichloropropane is widely used in industrial coatings (Li et al. 2016), lacquers, and varnishes (Vega et al. 2011), implying that the compound can be an indicator for the petrochemical industry.

The results for the Pearson's correlation analysis in all seasons are shown in Tables S3–6, in which three groups are shaded (strong: $r > 0.8$, good: $r = 0.6–0.8$, and negative: $r < -0.5$). Aromatic compounds showed relatively strong ($r >$

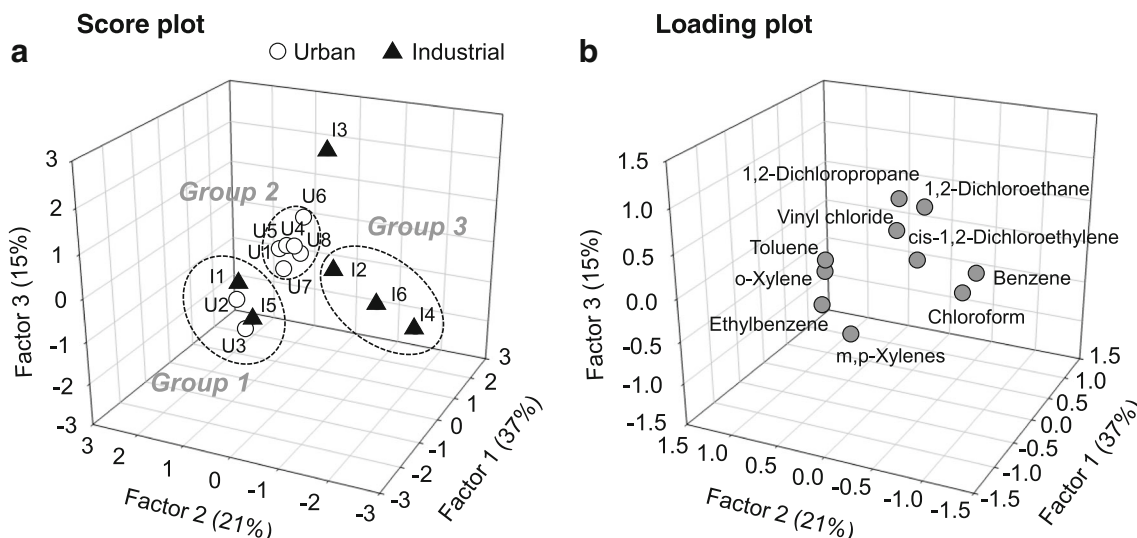


Fig. 6 Three-dimensional **a** score and **b** loading plots of the principal component analysis (PCA) in spring

0.8) and good ($r = 0.6–0.8$) correlations with each other except for benzene and styrene. Ethylbenzene and m,p-xylenes were strongly correlated ($r = 0.914, 0.968, 0.939$, and 0.962 in summer, fall, winter, and spring, respectively) as these two compounds were primarily emitted from the same source, the shipbuilding industrial complex.

In addition, a strong correlation ($r > 0.8$) was found between styrene and 1,2-dichloropropane in spring, summer, and fall, with these two compounds showing much higher concentrations at Site I3 except in winter, which implies that the compounds are indicators of emissions from the petrochemical industrial complex. Benzene and tetrachloroethylene, which are considered as industrial emission markers (Zhang et al. 2015), showed higher concentrations at Site I6 than at the other sites, and they were highly correlated in summer ($r = 0.818$) and spring ($r = 0.708$). In spring, vinyl chloride was negatively ($r < -0.5$) correlated with most other compounds, indicating that vinyl chloride might have different sources and emission patterns in Ulsan. In fall and spring, strong correlations ($r = 0.742–0.848$) were found between cis-1,2-dichloroethylene and trichloroethylene. Their concentrations were somewhat higher at Site I4 than at the other sampling sites, indicating that they could have been influenced by the use of metal degreasers (US-EPA 2001) in the non-ferrous industrial complex.

Conclusion

In this study, spatial and temporal variations of VOCs in Ulsan, Korea were examined using passive air samplers. The temporal variations of VOCs were not significantly different probably due to the continuous emissions from major industrial facilities. The spatial distributions of VOCs indicated that major industries, especially the petrochemical and shipbuilding industries,

were the main VOC sources. In addition to the industrial sites, some urban sites were also found to be significantly affected by VOCs emitted from the industrial complexes. Therefore, periodic monitoring of VOCs is recommended in Ulsan. It can be concluded that passive air sampling is a powerful tool for identifying major VOC sources in multi-industrial cities. In addition, the PRTR emission database developed by the Korea Ministry of Environment was found to be useful for source tracking and could also be used for the prediction of a source-receptor relationship without the need for monitoring and for input data of air dispersion models.

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