

Major aromatic VOC in the ambient air in the proximity of an urban landfill facility

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Abstract

In this study, the environmental behavior of major aromatic VOC (including benzene, toluene, ethylbenzene and xylene, commonly called BTEX) in the ambient air was investigated from a mid-size municipal landfill site located in Dae Gu city, Korea in the winter of 2004. A series of field campaigns were conducted in the course of the study to cover eight different locations within and near this landfill site along with a number of VOC vent systems. The mean concentrations of different VOC species in ambient air fell in a comparable range of at or above a few ppb (e.g., the most abundant toluene ~ 10 ppb). An inspection of the VOC data sets at the studied LF sites also indicated that they are quite analogous to those typically found in other urban areas in terms of their absolute magnitude and relative pattern (e.g., the general dominance of toluene over the other species). In light of the fact that there is active ventilation of landfill gas (LFG: e.g., with their LFG concentrations above a few to a few tens of ppm) in the study area with no other distinct source processes, it can be concluded that the effects of the landfill processes may be as important as other point sources in maintaining VOC concentration levels in certain urban areas.

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1. Introduction

As the final depository for most industrial and household wastes, the landfill (LF) facilities are often designated as intense sources of a wide range of trace pollutants including volatile organic compounds (VOC). The environmental significance of VOC is well known in various respects, e.g., their potential role in the formation of photooxidants [1,2] or in olfactory pollution [3,4]. Because of the significant influence on local and/or regional air quality, mitigation of landfill gas (LFG) emissions has often been viewed as an important element of LF emissions abatement research [5,6].

In the US, a total of 2300 landfill sites are reported to operate to dispose of up to 2.2×10^9 tonnes of waste annually (EPA,

2002 [7] and references therein); LFG emanation of VOC is hence estimated to constitute 10% of the VOC emissions occurring in the entire US. Hence, as a means of regulating VOC mitigations, more stringent measures have been introduced in the US such as the New Source Performance Standards (NSPS) in March 1996. Under the regulations of NSPS, all LF facilities with an annual emission rate above 50 Mg ($=10^6$ g) are forced to flare or to utilize LFG. In fact, enforcement of the stringent rules has effectively contributed to diminishing emissions of both greenhouse gases and VOC. In the case of Korea, a total of around 140 LF facilities are known to cover a sum of 1.1×10^8 tonnes of waste annually [8]; according to such report, 5/6 of wastes are of industrial origin, while 1/6 are from living facilities. It is nonetheless found that the landfilling rates of those two types of wastes differ greatly, as their proportion of burial corresponds to 12% and 40%, respectively. As in other countries, many stringent regulations have hence been introduced in Korea to reduce problems arising from waste treatment.

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Table 1

A statistical summary of relevant environmental parameters measured during our field campaign conducted in and around the Dae Gu landfill site (January 2004)

Parameter (unit)	Mean \pm S.D. (median)	Range (N)
(a) Meteorological parameters ^a		
WS (m s ⁻¹)	1.56 \pm 1.55 (1.00)	0.20–9.00 (801)
TEMP (°C)	-1.32 \pm 2.69 (-1.80)	-6.80 to 4.60 (801)
RH (%)	32.0 \pm 10.2 (30.0)	15.0–55.0 (801)
UV (MJ m ⁻²)	0.02 \pm 0.05 (0.00)	0.00–0.16 (801)
(b) Pollutant species		
NO (ppb)	8.80 \pm 18.5 (2.00)	1.00–149 (504/297) ^b
NO ₂ (ppb)	18.2 \pm 11.1 (17.0)	1.00–50.0 (796/5)
NO _x (ppb)	23.7 \pm 23.1 (19.0)	1.00–194 (797/4)
O ₃ (ppb)	20.1 \pm 10.6 (20.0)	1.00–43.0 (800/1)
SO ₂ (ppb)	5.85 \pm 4.80 (5.00)	1.00–20.0 (794/7)
CO (ppb)	0.33 \pm 0.18 (0.30)	0.10–0.90 (785/16)
CH ₄ (ppm)	73.2 \pm 26.0 (79.8)	17.6–104 (801)

^a Acronyms used for meteorological parameters denote: WS, wind speed; TEMP, temperature; RH, relative humidity and UV, ultraviolet radiance.

^b Number of the data after slash denotes the cases of which measurement data are recorded as zero value (or below detection limit); all statistics were made without considering these zero values.

In recognition of the strong potential for pollution from LF facilities and/or their operation, we conducted a field campaign to measure ambient VOC concentration levels from both in and around a municipal landfill site in the city of Dae Gu, Korea during the winter of 2004. For the purpose of this study, we investigated the spatio-temporal patterns of 10 individual VOC including benzene, toluene, ethylbenzene, and xylene (commonly called BTEX) from a total of eight different points in and around the landfill site. In addition to VOC, some other trace pollutants of environmental importance (e.g., CH₄, reduced sulfur compounds (RSC) and gaseous elemental mercury (GEM)) were also investigated concurrently. The results of RSC analysis have been reported in recent publications [9], while those of other target compounds including Hg will be reported elsewhere. The results of this field-based experimental campaign are thus used to explain the fundamental factors at work in the VOC distributions in the area under the influence of landfill processes and to explore their possible roles in governing the regional and/or local air quality.

2. Experimental

2.1. Site characteristics

In the present work, the concentrations of 10 VOC including BTEX were measured along with relevant environmental parameters from a municipal landfill site in Dae Gu, Korea (13–16 January 2004) (refer to Tables 1 and 2 for the list of parameters investigated in this study). The general characteristics of the studied LF site can be summarized as follows. It is located in the Bang Chun (BC) district in the city of Dae Gu with a distance of approximately 10 km west from the center of the city. As shown in Fig. 1, the studied area is placed in a relatively remote area surrounded by a small mountain with an elevation

of ~100 m. Because of this geographical location, it is not likely affected by other known sources. For instance, as it is about 3 km distance from major roads and/or highways, other major VOC sources (e.g., traffic activities) are not expected to exert direct influences on the studied LF area.

If one acknowledges the fact that there is an enormous LF site such as Nan Ji DO (NJD) in Korea (a total area of 2.76 km²: [10]), the target site can be ranked as of intermediate range with a total area and volume of 0.6 km² and 9.2 \times 10⁶ m³, respectively (Fig. 1). It has been built and operated since 1990, and pre-sanitization treatment is strictly applied to the wastes before burial. The amount of landfill wastes buried in the target LF, while consisting mainly of household wastes, was estimated to be 1900 tonnes per day (in the year 2003). The LF site has an oval shape with a tilted slope (~15°). The working face was located in the bottom half so that the lowest point is placed near the LF entrance. To facilitate LFG flaring, the LF management team installed and operated a total of about 80 vent pipes on a routine basis. Because the upper half of LF is the most stabilized, most vent pipes are installed on the upper side. In fact, the construction of these ventpipes and the flaring were employed as the most efficient method of olfactory pollution control in this LF environment.

To study the possible influence of strong sources on the distribution patterns of VOC in the ambient air, we selected a total of eight sampling locations in our study area for the measurements of VOC (Fig. 1). These eight locations were selected to include: (1) a small residential facility approximately 1 km from the entrance of the LF site (site no. 1), (2) an entrance point to the LF facility (site no. 2), (3) one near the central part of the LF area (site no. 8) and (4) five points at the borderline LF facilities (site nos. of 3–7).

2.2. The collection and analysis of VOC samples

In order to evaluate VOC distributions in the LF environment, their concentration levels were measured from both ambient air and LFG. As the analysis of LFG composition in the study area has been made for many trace gases including reduced sulfur gases and VOC [11], we confined the analysis of these LFG data to help explain the behavior of ambient VOC. The number of target analytes investigated in this study corresponds to a total of 10 individual VOC, as shown in Table 2. To simplify the comparison of the data, a detailed analysis of VOC concentrations was mainly directed to six major aromatic components of VOC, i.e., BTEX. Hence, the distribution characteristics of VOC were presented and discussed in the following sections mainly in terms of BTEX compounds. These major aromatic components are commonly viewed as constituting 20–40% of non-methane hydrocarbons (NMHCs) in urban areas [12,13].

In this study, measurements of aromatic VOC in ambient air were basically planned and conducted at twice-per-day intervals (i.e., daytime and nighttime) from all eight sampling locations during a 4-day study period (13–16 January 2004). The schedule for the twice daily sampling was adjusted so that daytime sampling was made between 10:00 and 11:00 a.m., while the

Table 2
A statistical summary of VOC measured in and around the landfill site during the entire study period (13–16 January 2004)^a

Site no.	BEN ¹	TOL ²	EB ³	MPX ⁴	STR ⁵	OX ⁶	BrB ⁷	1,3,5-TMB ⁸	1,2,4-TMB ⁹	p-IPT ¹⁰
(A) The concentrations of VOC in ambient air (in ppb unit)										
1	0.82 ± 0.45 (0.70) ^a 0.36–1.59 (6) ^b	7.54 ± 3.58 (8.41) 1.30–11.2 (6)	2.25 ± 2.48 (1.68) 0.49–7.15 (6)	0.43 ± 0.43 (0.31) 0.12–1.28 (6)	0.21 ± 0.23 (0.14) 0.04–0.65 (6)	0.15 ± 0.18 (0.08) 0.04–0.52 (6)	0.20 ± 0.09 (0.20) 0.14–0.26 (2)	1.33 ± 0.35 (1.16) 1.10–1.73 (3)	0.41 ± 0.26 (0.35) 0.14–0.85 (6)	1.62 ± 2.18 (0.70) 0.10–5.94 (6)
2	0.20 ± 1.09 (0.69) 0.52–3.12 (5)	6.40 ± 5.28 (6.22) 1.04–13.1 (5)	1.29 ± 0.95 (1.04) 0.49–2.80 (5)	0.24 ± 0.16 (0.15) 0.12–0.51 (5)	0.18 ± 0.09 (0.15) 0.07–0.29 (5)	0.08 ± 0.03 (0.08) 0.04–0.10 (5)	0.10 ± 0/1 (0.10) 0.10–0.10 (2)	2.31 ± 1.90 (2.31) 0.96–3.65 (2)	0.24 ± 0.14 (0.26) 0.08–0.39 (5)	0.55 ± 0.50 (0.41) 0.07–1.39 (5)
3	0.66 ± 0.34 (0.60) 0.32–1.13 (4)	5.50 ± 6.45 (2.96) 1.22–14.9 (4)	3.93 ± 5.82 (1.35) 0.41–12.6 (4)	0.75 ± 1.15 (0.22) 0.08–2.47 (4)	0.27 ± 0.35 (0.12) 0.05–0.79 (4)	0.08 ± 0.05 (0.08) 0.02–0.13 (4)	0.18 ± 0.13 (0.18) 0.09–0.28 (2)	2.40 ± 2.45 (2.40) 0.67–4.14 (2)	0.54 ± 0.80 (0.16) 0.10–1.74 (4)	5.00 ± 8.21 (1.32) 0.09–17.3 (4)
4	0.65–0.23 (0.68) 0.42–0.97 (5)	6.84 ± 3.89 (8.08) 2.00–11.9 (5)	2.61 ± 2.31 (1.60) 0.94–6.50 (5)	0.57 ± 0.62 (0.27) 0.16–1.64 (5)	0.39 ± 0.50 (0.15) 0.06–1.25 (5)	0.15 ± 0.17 (0.08) 0.06–0.45 (5)	0.09 ± 0.08 (0.09) 0.04–0.15 (2)	3.55 –	0.19 ± 0.08 (0.19) 0.09–0.30 (5)	2.83 ± 4.46 (0.63) 0.32–10.8 (5)
5	0.68–0.30 (0.67) 0.39–1.16 (5)	6.98 ± 3.82 (7.23) 3.35–12.4 (5)	1.47 ± 0.72 (1.13) 0.76–2.29 (5)	0.29 ± 0.14 (0.24) 0.16–0.48 (5)	0.13 ± 0.06 (0.12) 0.07–0.22 (5)	0.11 ± 0.10 (0.06) 0.05–0.28 (5)	0.15 ± 0.08 (0.15) 0.10–0.21 (2)	–	0.17 ± 0.08 (0.16) 0.08–0.30 (5)	0.72 ± 0.78 (0.37) 0.18–2.07 (5)
6	1.73 ± 2.45 (0.79) 0.39–6.69 (6)	8.02 ± 6.06 (5.66) 2.22–16.3 (6)	2.28 ± 1.15 (2.38) 0.72–4.11 (6)	0.38 ± 0.17 (0.37) 0.15–0.61 (6)	0.11 ± 0.05 (0.10) 0.05–0.19 (6)	0.16 ± 0.12 (0.11) 0.08–0.41 (6)	0.06 ± 0.03 (0.06) 0.03–0.10 (4)	1.48 ± 1.52 (1.48) 0.40–2.55 (2)	0.40 ± 0.49 (0.12) 0.08–1.31 (6)	0.81 ± 0.67 (0.56) 0.16–1.93 (6)
7	1.27 ± 1.24 (0.76) 0.43–3.73 (6)	13.0 ± 5.31 (14.1) 2.58–17.5 (6)	3.24 ± 1.41 (3.78) 0.85–4.44 (6)	0.56 ± 0.24 (0.61) 0.18–0.81 (6)	0.24 ± 0.14 (0.19) 0.15–0.51 (6)	0.14 ± 0.06 (0.13) 0.05–0.22 (6)	0.12 ± 0.07 (0.11) 0.06–0.22 (4)	3.27 ± 3.46 (1.66) 0.90–7.24 (3)	0.30 ± 0.25 (0.23) 0.13–0.81 (6)	0.84 ± 0.85 (0.62) 0.16–2.53 (6)
8	0.69 ± 0.32 (0.60) 0.47–1.33 (6)	12.5 ± 4.73 (12.7) 4.51–17.7 (6)	2.96 ± 1.06 (3.25) 1.32–4.12 (6)	0.55 ± 0.19 (0.57) 0.28–0.80 (6)	0.27 ± 0.12 (0.25) 0.15–0.46 (6)	0.18 ± 0.06 (0.20) 0.08–0.26 (6)	0.07 ± 0.04 (0.05) 0.04–0.12 (4)	1.89 ± 1.64 (1.20) 0.37–4.60 (5)	0.34 ± 0.19 (0.26) 0.12–0.62 (6)	1.11 ± 1.12 (0.8) 0.25–3.31 (6)
Mean ^b	0.99 ± 1.10	8.58 ± 5.26	2.49 ± 2.22	0.46 ± 0.44	0.22 ± 0.23	0.13 ± 0.11	0.11 ± 0.07	2.18 ± 1.82	0.32 ± 0.35	0.15 ± 0.11
(B) VOC concentration in vent system (in ppm unit)										
Vent	1.36 ± 0.83 (1.30) 0.13–2.73 (14)	64.8 ± 74.4 (28.9) 0.41–253 (14)	12.6 ± 7.31 (13.1) 1.47–22.8 (14)	2.04 ± 1.22 (2.13) 0.22–3.85 (14)	0.57 ± 1.12 (0.28) 0.02–4.44 (14)	0.50 ± 0.37 (0.54) 0.03–1.00 (14)	0.14 ± 0.07 (0.11) 0.06–0.27 (12)	5.34 ± 3.74 (4.84) 1.21–11.8 (10)	0.45 ± 0.45 (0.37) 0.11–1.83 (14)	2.34 ± 1.61 (1.80) 0.40–6.12 (14)

Superscripts (1)–(10) denote benzene, toluene, ethylbenzene, *m,p*-xylene, styrene, *o*-xylene, bromobenzene, 1,3,5-trimethylbenzene, 1,2,4-Trimethylbenzene and *p*-Isopropyltoluene, respectively. Letters 'a' denotes the mean and 1S.D. with the median value, while 'b' denotes range between minimum and maximum with a total number of observations (*N*).

^a The results are compared for both ambient air data collected from eight locations along with LFG samples.

^b Mean values are derived using all data sets.

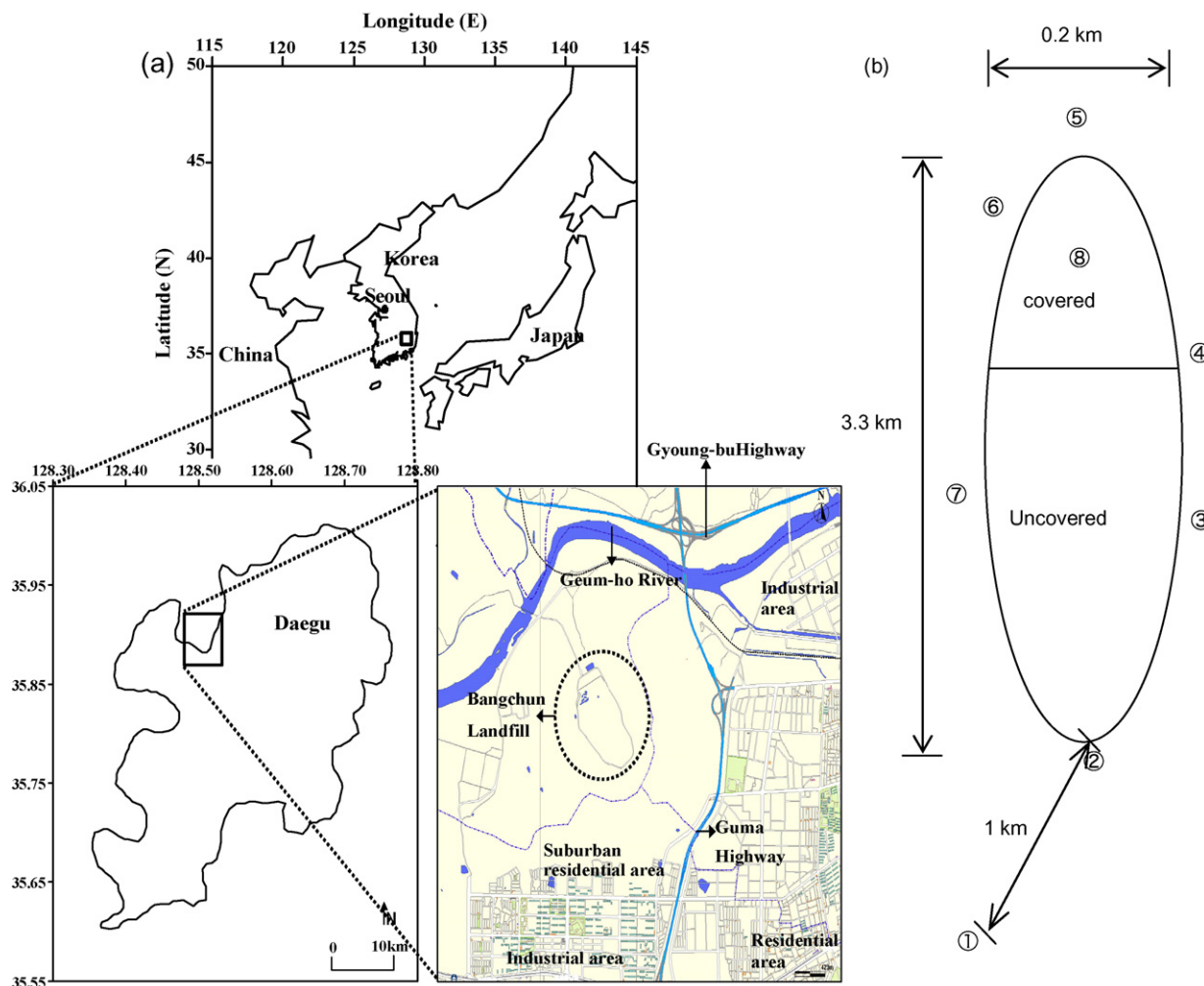


Fig. 1. Location of sampling points ($35^{\circ}52'07''$ and $128^{\circ}31'00''$) in a municipal landfill area of Daegu, Korea. Each site is selected to represent both within and outside the LF area (site 1 = residential area; site 2 = near the landfill gate; sites 3–7 = circumference of landfill; site 8 = a center of the upper portion in the landfill area).

nighttime sampling was between 14:00 and 15:00 p.m. The collection of each air sample between the two time periods of the day was replicated using a 10-L capacity Tedlar bag sampler. All of these samplings were basically made with the aid of a box-shaped, vacuum-driven lung sampling system at a mean sampling flow rate slightly exceeding 2 L min^{-1} (total sampling time of less than 5 min). In addition, Tedlar bags containing ultrapure N_2 were brought back and forth between field and lab and used to measure blank levels of VOC analysis. For the comparative purposes, on certain occasions, the collection of VOC samples was also made side-by-side by adsorption tubes filled with a Tenax adsorbent. The results of this comparative analysis between the two sampling methods indicated that there was fairly excellent agreement (e.g., 95%) from a number of VOCs (including toluene, ethylbenzene and xylene). However, some differences (up to 30%) were seen from light VOCs like benzene (loss due to insufficient affinity of the sorbent) or from a few heavy VOCs (e.g., above C8 compounds: due to bag wall adsorption loss). As a number of artifacts can be involved in the sampling or analysis of VOC, all VOC data for this study were basically derived by sampling and calibration against the

bag sampling method. To facilitate the comparison of our measurement data, we assumed that the loss of certain VOC due to the bag sampling method was comparable between the standard and field samples. As a detailed discussion of such subject is the beyond the scope of this study, it will be outlined in future publications.

The samples collected from the field campaign were then brought into the laboratory within 24 h and analyzed with the GC/FID system combined with Peltier cooling (PC) and thermal desorption (TD) units (Markes International, Ltd., UK). This PC/TD system was then operated in the following sequence: (1) initial TD of tube samples at 350°C for 5 min; (2) focus (PC stage) of VOC on a cold trap at -30°C ; (3) secondary TD at 300°C for 5 min (note that step (1) can be omitted for samples collected in a Tedlar bag). The cold trap used in the PC stage was prepared by packing two types of adsorbents—Carbopack BTM and CTM (both in 60/80 mesh) on a 1:2 weight ratio. The pressurized gas streams containing those thermally desorbed VOC were subsequently introduced into the flame ionization detector (FID) of our GC system (Model 6200, Donam Instrument Co., Korea). Those transported VOC were then separated on a DB-

VRX column (60 m × 0.32 mm × 1.8 μm, J&W) and detected by the FID detector. The GC/FID system, while being held at the flow rates of 30 mL min⁻¹ (N₂ and H₂) and 300 mL min⁻¹ (air), was operated under the following temperature conditions: 200 (injector), 50 (oven) and 250 °C (detector).

The precision of the VOC analysis, if quantified individually by triplicate analysis of standard, varied among different species but was generally in a few % range (3–9%). The accuracy of our measurement method was also estimated by comparing the concentrations of the gravimetrically prepared standards (using three different solution mixture types: UST BTEX mix, EPA VOC Mix 2 and EPA 524 VOC Mix A) against gaseous standards diluted to the desirable range from commercially purchased, highly concentrated ones (Restek, alpha, NJ, USA). We were able to find a fair agreement (less than a few percent range in general) in the BTEX concentration levels between two standard types. The detection limit of those aromatic VOC was commonly achieved at the 0.1 ng level.

3. Results and discussion

3.1. The overall picture of VOC distribution in the LF area

To examine the fundamental aspects of VOC distributions at our study site, a number of relevant environmental parameters were investigated in relation with the VOC data sets (Table 1); measurements of these parameters were made from the central area of the landfill site using a mobile van equipped with an automatic weather monitoring system (near measurement point no. 8 in Fig. 1). The basic meteorological conditions that prevailed during the study period are plotted as a function of time in Fig. 2.

The general meteorological conditions during the study period may be described best by parameters related with wind rose patterns. In the morning, northerly winds (315–45°) were dominant (~50% of sampling period) with relatively low wind speeds (1.1 ± 0.5 m s⁻¹). In the afternoon, northerly wind became predominant (90%), and wind speed increased by a factor of 3. UV radiation in the morning (0.092 ± 0.013 mW cm⁻²) was higher than that in the afternoon by a factor of 7. Differences in air temperature between morning (−1.2 ± 1.4 °C) and afternoon (1.8 ± 1.9 °C) were 3 °C, while relative humidity (RH) in the afternoon slightly decreased from 32% to 21%. There was no precipitation and partly cloudy (cloud covering less than 4/8) or clear skies were observed.

A unique feature of our study was the fact that the mean atmospheric concentrations of methane measured during the study period generally approached abnormally high values of 73 ppm. This concentration level of CH₄ is dramatically higher than that of the ambient air (e.g., typically in ~2 ppm level: [14,15]) and also far higher than those of other LF sites by about an order of magnitude (e.g., [16]). Landfilling processes were in fact identified as the main source of CH₄ in the metropolitan area of the city [14,17,18] and estimated to account for 6–12% (35–73 T_g CH₄ year⁻¹) of the global anthropogenic emissions of CH₄ [19].

The results of our VOC analysis are summarized in Table 2. If we compare the magnitude of concentration among different VOC, toluene exhibits the largest value, followed by ethylbenzene, *n*-butylbenzene, 1,2,4-trimethylbenzene and so on. It is found that toluene generally records the highest value of around 10 ppb, while the concentrations of other VOC were typically found to be around 1 ppb. To briefly examine the relationships

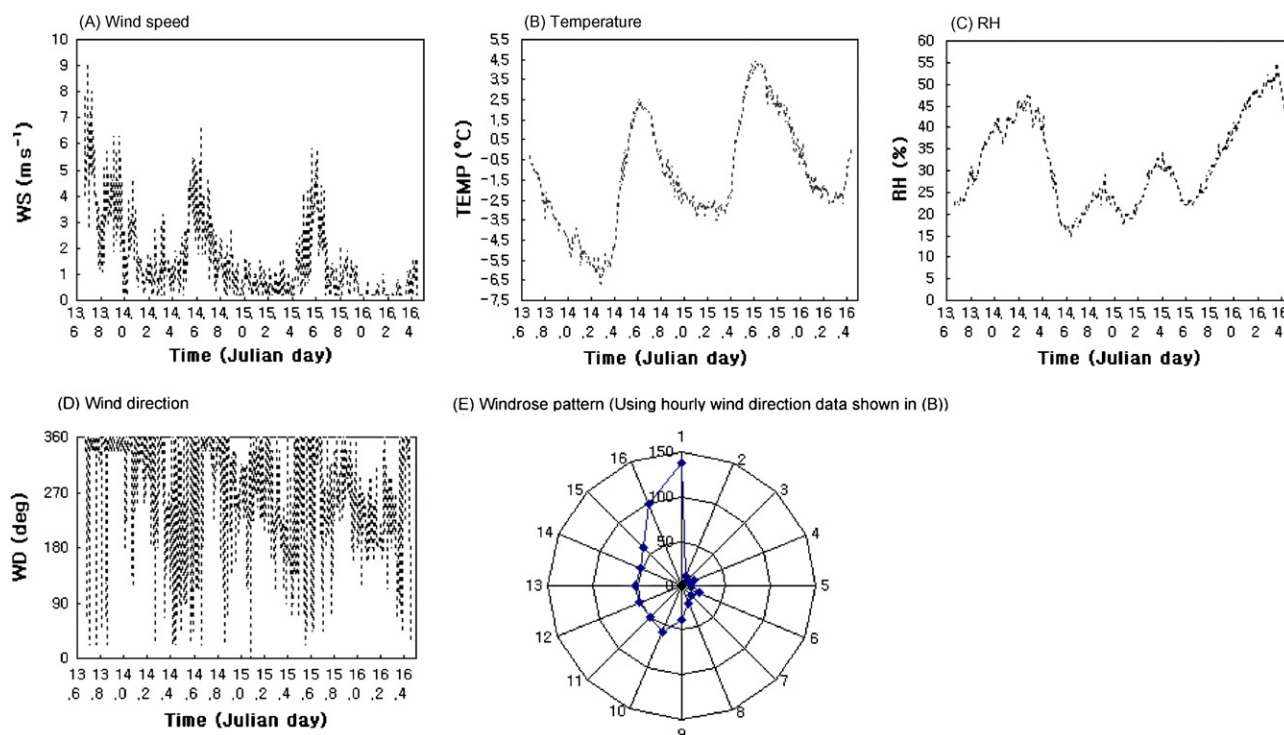


Fig. 2. Temporal variation patterns of the basic meteorological parameters measured during the entire study period.

between ventilation source processes and their effects on ambient VOC concentrations, our measurement data were compared further with those collected from infiltrated vent pipes during the same study period (Table 2). The results of this comparison generally indicate significant differences in concentration levels between the two different sample types.

Although the differences in concentration levels between LFG and ambient air correspond to approximately 10^4 times (e.g., toluene), the relative distribution patterns between the two sample types are generally comparable to each other. For instance, as a means of indirectly examining the source characteristics of VOC, the concentration ratio between different VOCs can be computed and compared against the highest component, toluene such as VOC/toluene (V/T) ratio. The results of this comparison indicate that the concentration of benzene measured from ventpipes is substantially lower than that of ambient air (such as B/T ratio of 0.02 (LFG) versus 0.12 (ambient air)), while differences are not that significant for most other VOCs. In fact, the anomalous deficiency of benzene can also be assessed by the mean concentration ratio of each compound between LFG and ambient air such as L/A ratio. It is found that the computed L/A ratio of BTEXS decreases on the order of toluene (7.55×10^3), ethylbenzene (5.06×10^3), *m,p*-xylene (4.43×10^3), *o*-xylene (3.85×10^3), styrene (2.59×10^3) and benzene (1.37×10^3). If one considers the observed differences in the computed concentration terms—whether being V/T or L/A ratios, relative depletion of benzene appears to be a prominent process in the study area. It is, however, noteworthy that relative patterns of ambient VOC in the studied LF area are not unusually different from those seen in other urban areas (e.g., [20]). Hence, the observed depletion phenomenon is suspected to come from its depletion in LFG component rather than in other compartments. Although more studies are desirable to account for the cause of such phenomenon, one can assume that there may be a certain process which can lead to a relative depletion of benzene during the LFG formation.

In light of the fact that the study landfill site is fairly distant from traffic or other source processes, it is most reasonable to infer that the VOC levels of the surrounding area are by and large affected by landfill processes. However, if one considers the fact that these observed VOC levels are not clearly distinguished from those commonly seen in moderately polluted urban areas, the active emanation of VOC from the landfill environment may not necessarily enhance the VOC concentrations much higher than other anthropogenic sources including traffic activities. This is not overly unrealistic, if one refers to the finding that vehicular exhaust is the major source of measured ambient VOC in urban air, while LF is one of the minor sources such as asphalt and paints [21].

As a means to explain the factors controlling ambient VOC distributions in a strong source environment, correlation analysis was conducted by combining the measurement data for all major VOC (2 sampling (per day) for 3 days from 8 points: $N=48$) (Table 3). The results indicate that the cases of strong correlations are seen fairly abundantly across many matching pairs. Out of 21 matching pairs, the sum of 12

Table 3

Results of correlation analysis between major aromatic VOCs measured from landfill environments in Bang Chun (BC) landfill site, Dae Gu, Korea^a

	TVOC	BEN	TOL	EB	<i>m,p</i> -X	STR	<i>o</i> -X
TVOC	1						
BEN	0.36	1					
TOL	0.78 ^{III}	0.48 ^I	1				
EB	0.75 ^{III}	0.09	0.55 ^{II}	1			
<i>m,p</i> -X	0.70 ^{III}	0.07	0.48 ^I	0.98 ^{III}	1		
STR	0.47 ^I	0.04	0.25	0.74 ^{III}	0.82 ^{III}	1	
<i>o</i> -X	0.33 ^I	0.04	0.36 ^I	0.21	0.18	0.07	1

Superscripted Roman letter symbols of I–III denote the cases with the probability of no correlation less than 10^{-3} , 10^{-4} and 10^{-5} , respectively.

^a For this analysis, all data collected from eight measurement sites were combined ($N=8$ sites \times 6 measurements for a 3 day period = 48).

correlated pairs is found to be statistically significant (at probability of no correlations below 10^{-3}). It is interesting to note that, as shown in Table 3, the strength of correlation is distinguished greatly between compounds; whereas some compounds (toluene, ethylbenzene and xylene) tend to exhibit fairly strong correlations, other do not (benzene and styrene). Hence, the results of correlation analysis suggest that relative behavior of VOC emanating from LF can be distinguished to a certain degree despite their similarities in physicochemical properties.

3.2. The spatial distribution patterns of VOC in and outside the landfill site

As our measurement points were placed to cover both in and outside the landfill site, it may be useful to describe the spatial distribution characteristics of our VOC measurement data. If one considers that some aromatic VOC (like BTEX and styrene) may be used as an odorous indicator, information concerning their spatial distribution patterns can be important in accounting for the effect of landfill processes on the surrounding environment. As shown in Fig. 1, site no. 1 is located in an apartment complex area approximately 1 km away from the landfill site. However, all the other sites are at or within the landfill boundary (such as site nos. 2–8). Hence, it is reasonable to expect that the direct influence of landfill site may be reflected less sensitively at site no. 1 than the others.

To check for the inter-site variabilities of VOC distribution patterns, the VOC concentrations are plotted as a function of site number in Fig. 3. A rough comparison of these data suggests that the most dominant VOC, toluene can alone account for approximately 30% of TVOC. Note that TVOC concentration terms are derived based on ppbC concept, although expressed as ppb (like other VOCs) in Figs. 3 and 4; hence, 1 ppb benzene corresponds to 6 ppbC TVOC because of six carbons in the benzene ring. (For reference, ppbC is computed by assuming the molecular weight of an unknown mixture simply as a single carbon.) The results, however, indicate that their spatial distribution patterns are not simple enough to describe. Despite the isolated location, the VOC concentration levels at site no. 1 are not significantly different from the patterns of all the other sites. In addition, it is

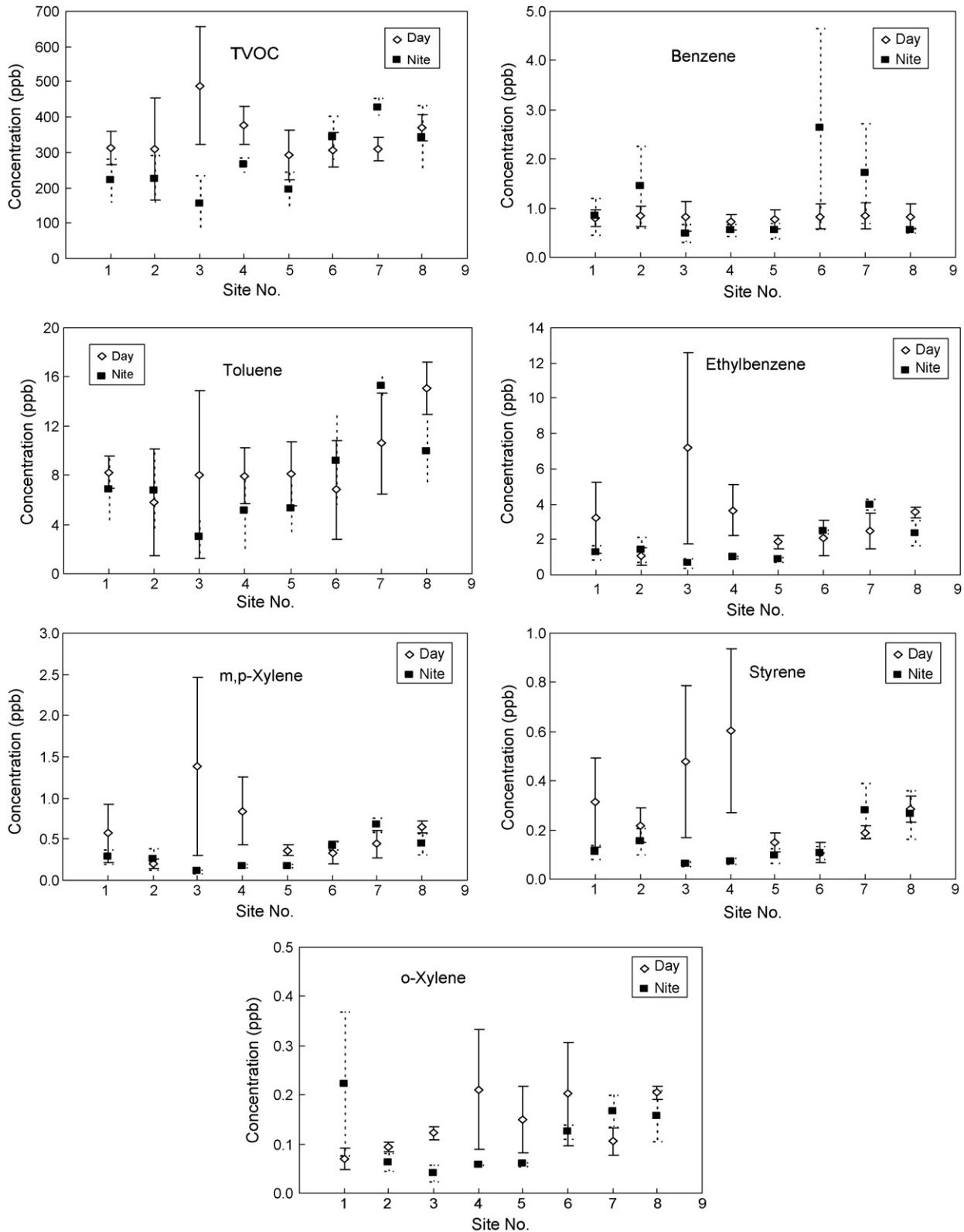


Fig. 3. Comparison of ambient VOC concentration levels between sites and diurnal periods.

found that except for toluene, the concentrations of most VOC, measured at the site of the most strong source effect (i.e., site no. 8 near the central LF area), are not distinguished statistically from those measured at other sites (Fig. 3).

Although it is difficult to account for the observed differences between the site no. 3 and others, we suspect that such differences are by and large due to the presence of a management office building and related facilities near site no. 3. It is interest-

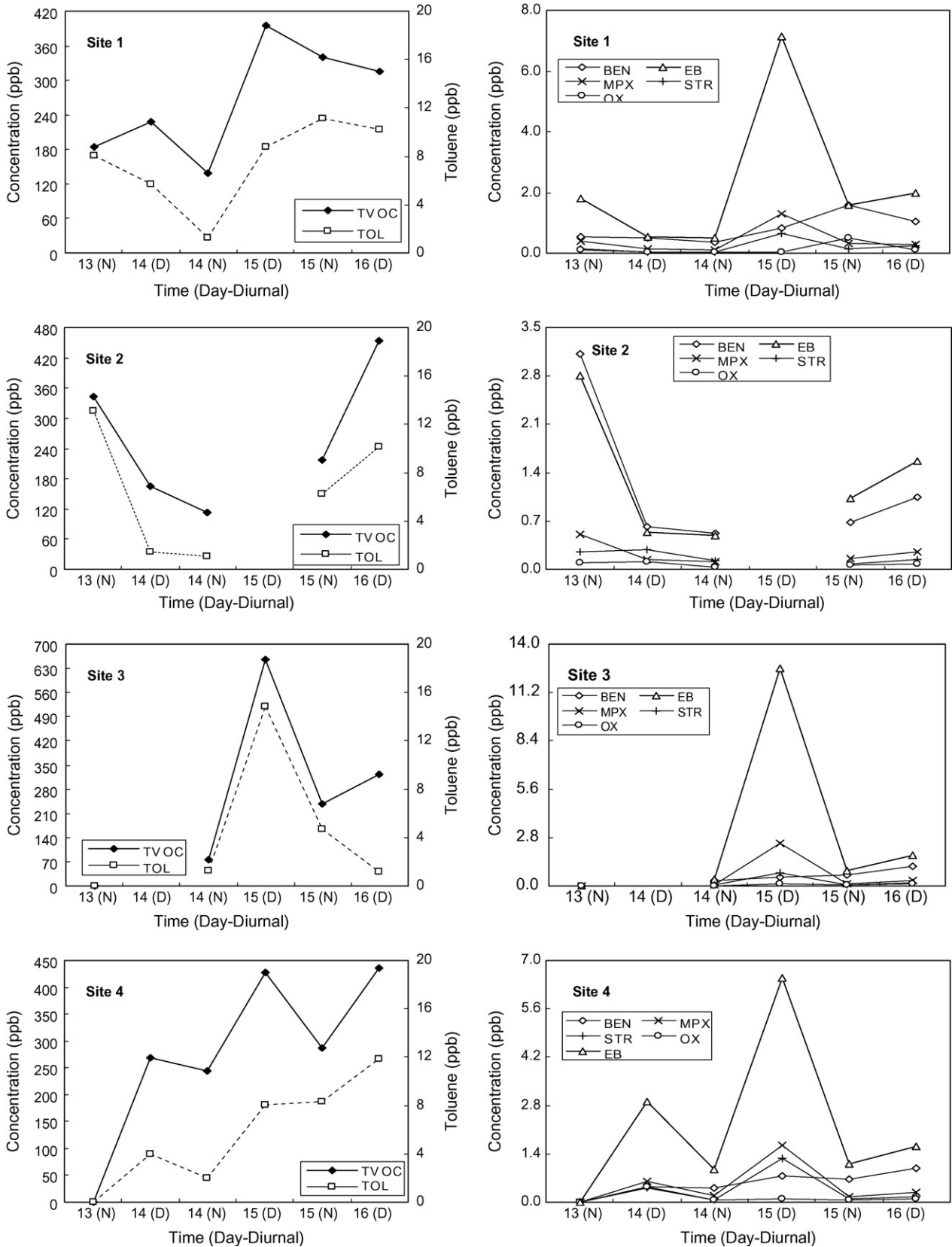


Fig. 4. Plots of temporal distribution patterns of TVOC and BTEX across the whole study period. Capital letters of D and N on the x-axis denote day and night measurements, respectively. Refer to the annotations of Table 2 for the abbreviated terms of VOC.

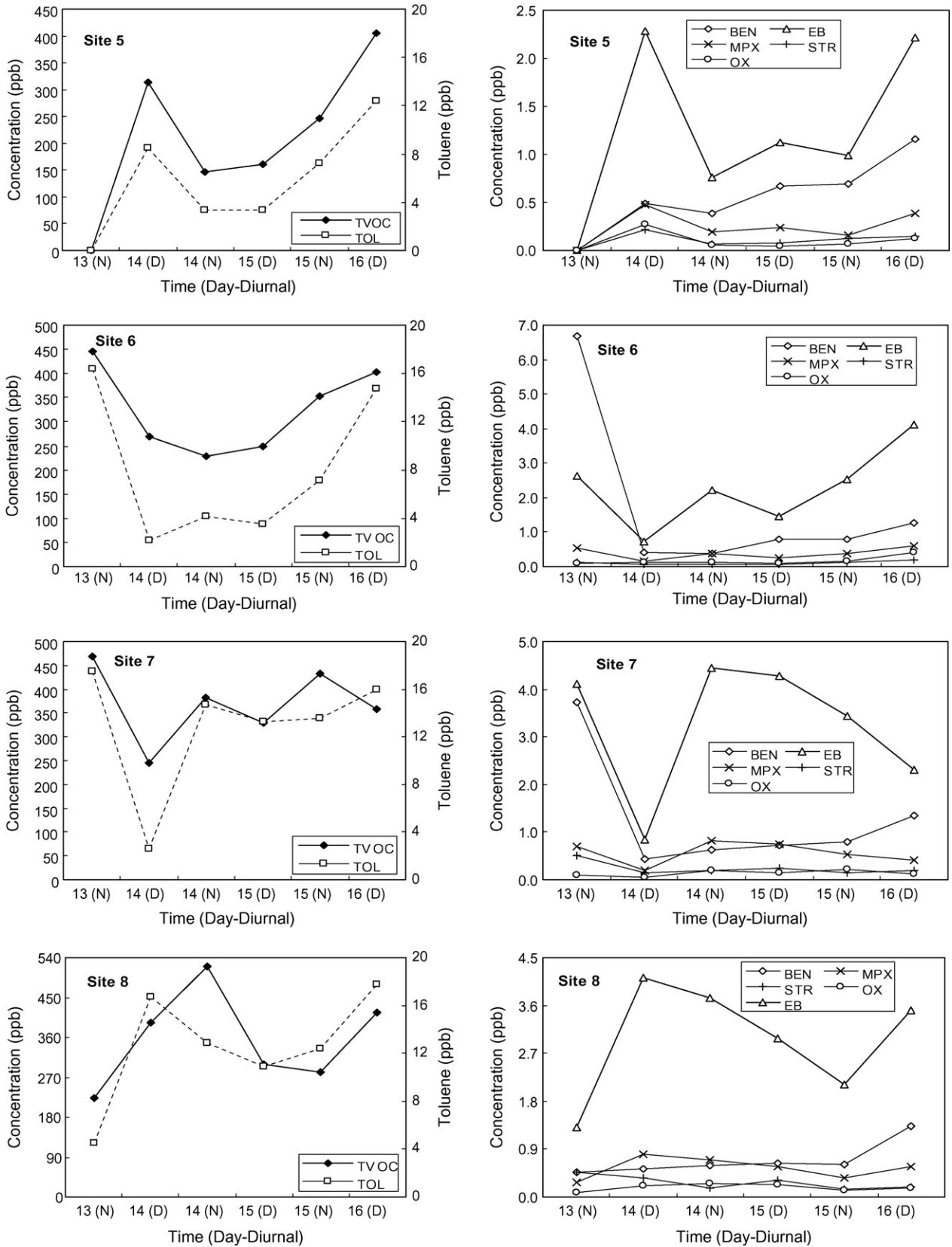


Fig. 4. (Continued).

ing to note that the results measured at site no. 3 are distinctive enough to show significant variations for most VOC, including BTEX and styrene, compared to other sites. Despite the fact that substantial quantities of VOC are emanated via ventilated pipes (or as surface seeping), the general compatibility in concentration levels between a small residential site (site no. 1) and most of the landfill sites suggest that the study landfill facility may exert some influences on the VOC levels in this relatively secluded area. In addition, it should be recalled that styrene concentration levels in the study area are high enough to be distinguished from those commonly seen in vehicular exhausts; hence, the constant observations of relatively high styrene concentrations also suggest the role of LF emissions in controlling VOC levels in the surrounding area.

3.3. Temporal distribution of ambient VOC in the surrounding areas of the landfill site

In Fig. 4, the temporal distribution of ambient VOC data is examined using our data sets collected from all eight different sampling locations over the entire study period. The results of the benzene data sets indicate that the temporal patterns are quite consistent through time among most sampling locations. They exhibited systematically high concentrations at the beginning of the study period, but showed a consistent drop from the second day at most study locations. Our observations of the relative temporal pattern may reflect the effect of local windrise pattern and atmospheric stability by which dispersion of pollutants are controlled to a degree.

Although the occurrence of the peak concentrations generally differ from each other for many VOC species (e.g., ethylbenzene, *m,p*-xylene and styrene), the maximum values of site nos.

1, 3 and 4 were found concurrently during the daytime on 15 January. As the analysis of wind direction data have shown, a number of sites (1–4) can better represent the downwind positions, especially during the afternoon time. In fact, the afternoon period of 15 January is recorded to show a fairly strong shift in many meteorological parameters (e.g., in the middle of a drastic increase in windspeed and temperature) under the prevailing northerly winds.

Considering that all measurements are made across day and night periods, diurnal variation patterns can also be examined for each individual sampling location. However, because of limited data sets obtained during this study, an explanation of such temporal trends should be made with a caution. In Fig. 3, their distribution patterns are compared with the day, night and all data sets (i.e., without grouping them). The results of this comparison indicate that there exist certain spatial patterns between sites so that the VOC levels measured from such a site as no. 3 tend to be more variable than the others. It is also found that a number of compounds including toluene consistently show relatively enhanced concentrations during daytime at some of the locations (such as site nos. 1, 3–5). In contrast, the diurnal patterns for benzene appear to be complicated enough in this respect. To check for the significance of those concentration differences across day and night periods, we conducted a *t*-test at each individual site between the day and night periods (Table 4). If the results are compared at the confidence level of 10%, differences in concentration levels between the two time periods are not distinctive enough for most examined sites. As shown by the results of this *t*-test, it is difficult to expect systematic differences in day–night VOC patterns; this observation thus suggests the possibility that the investigated environments may be affected incessantly by a constant local source like the studied LF site.

Table 4

Results of a statistical test to check for the significance of concentration levels of different VOC measured between day (10:00–11:00 a.m.) and night periods (16:00–17:00 p.m.) from a total of eight different sampling locations investigated in this study

Site no.	TVOC		BEN		TOL		EB		MPX		STR	
	<i>t</i> -value	<i>P</i> ^a	<i>t</i> -value	<i>P</i>	<i>t</i> -value	<i>P</i>	<i>t</i> -value	<i>P</i>	<i>t</i> -value	<i>P</i>	<i>t</i> -value	<i>P</i>
1	1.19	0.3	0.1	0.93	0.44	0.68	0.95	0.4	0.77	0.48	1.1	0.33
2	0.61	0.58	0.55	0.62	0.18	0.87	0.39	0.72	0.36	0.74	0.77	0.5
3	1.81	0.21	0.98	0.43	0.72	0.55	1.21	0.35	1.18	0.36	1.34	0.31
4	1.55	0.22	0.77	0.5	0.75	0.51	1.4	0.26	1.24	0.3	1.23	0.31
5	0.98	0.4	0.82	0.47	0.77	0.5	2.04	0.13	2.07	0.13	1.04	0.38
6	0.44	0.68	0.87	0.43	0.45	0.68	0.35	0.75	0.58	0.59	0.01	0.99
7	2.78	0.05	0.84	0.45	1.09	0.34	1.46	0.22	1.3	0.26	0.78	0.48
8	0.29	0.79	1.05	0.35	1.49	0.21	1.47	0.21	1.37	0.24	0.18	0.87

Site no.	OX		BrB		1,3,5-TMB		1,2,4-TMB		<i>p</i> -IPT	
	<i>t</i> -value	<i>P</i>	<i>t</i> -value	<i>P</i>	<i>t</i> -value	<i>P</i>	<i>t</i> -value	<i>P</i>	<i>t</i> -value	<i>P</i>
1	1.03	0.36	–	–	–	–	0.02	0.98	0.69	0.53
2	1.28	0.29	–	–	–	–	0.6	0.59	0.84	0.46
3	3.83	0.06	–	–	–	–	1.17	0.36	0.99	0.43
4	0.96	0.41	–	–	–	–	1.33	0.28	0.66	0.55
5	1.04	0.37	–	–	–	–	0.93	0.42	0.93	0.42
6	0.72	0.51	–	–	–	–	0.49	0.65	0.7	0.52
7	1.44	0.22	–	–	–	–	0.92	0.41	0.96	0.39
8	0.87	0.43	–	–	–	–	1.06	0.35	0.42	0.7

^a Denotes the probability that their differences are not significant between daytime and nighttime period for a comparison pair.

4. Conclusion

In this work, the VOC concentrations in ambient air were measured at a landfill facility located in the city of Dae Gu during a short period in January 2004. The results of this study indicate that the concentration levels of VOC are significantly differentiated between the ambient air and ventilated pipes. Although, the ambient concentration of certain VOC (such as toluene) was found at around 10 ppb, its LFG counterpart was seen to be as high as a few tens of ppm. In addition, the distribution patterns of ambient VOC were also examined in terms of spatial factors by comparing their concentration levels across all eight different sampling locations. It was observed that their concentration levels were not significantly different between nearby residential areas and the central part of landfill site. The results of our VOC analysis, when compared between day and night periods, also indicated that their distribution patterns are not clearly distinguished diurnally from most sampling locations with similar characteristics. It is thus necessary to consider the fact that the ambient VOC levels in the studied LF area are rather compatible with those typically observed in other polluted urban areas.

In light of the fact that there are no other prominent sources to affect the VOC levels in the study area under relatively secluded conditions, LF processes may be considered as the most important source to control VOC distribution in the surrounding area. The observed pattern of VOC in the studied LF facilities, however, contrasts slightly with other major LF pollutants such as ambient CH₄; there is a line of evidence that the concentrations of CH₄ in the urban air can be affected more significantly by LF activities. It is thus more likely to expect that the landfill processes in the study area may lead to the occurrences of strong VOC emission, and yet its effects are not significantly different from other prominent source processes in the urban environment.

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