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Comparative analysis of bias in the collection of airborne pollutants: Tests on major aromatic VOC using three types of sorbent-based methods

Ki-Hyun Kim*, Sang-In Oh, Ye-Jin Choi

Department of Earth & Environmental Sciences, Sejong University, Goon Ja Dong 98, Seoul 143-747, South Korea

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Abstract

This study was undertaken to establish one of the most reliable sampling methods and to precisely evaluate the bias involved in the collection of airborne pollutant samples. For the purpose of our study, we investigated the performance of three different types of sampling techniques by measuring major aromatic volatile organic compounds (VOC) in outdoor air; the target analytes specifically include benzene, toluene, ethylbenzene, and xylene (commonly called BTEX). As the first step of our approach, we designed and developed a multi-channel sampling system consisting of a six-port mass flow controller (SJU-MFC) system. Because this system allowed the collection of up to six replicate samples, our measurement results were analyzed and screened statistically for the derivation of high-quality BTEX data. The feasibility of this sampling system was further tested through a comparison with concurrent measurement data sets obtained by two additional, but independent, sampling techniques: (1) automatic continuous sampler (ACS) and (2) on-line GC (O-GC) system. Based on the data sets collected concurrently by three different sampling methods, we attempted to evaluate the compatibility of sampling techniques. Although the results obtained by SJU-MFC system were not statistically different from those of the O-GC system, they were moderately distinguishable from those of ACS. Such patterns were seen consistently, when examined by correlation analysis. The overall results of our study thus generally point out that the compatibility of data sets, when the proper caution is taken, improve significantly among different sampling methodologies.

Keywords: VOC; BTEX; Precision; Mass flow controller; On-line GC

1. Introduction

Due to the notable improvement achieved in the development of sampling techniques and modern instrumentation over the past decades, subtle changes in the concentration of various airborne pollutants can be detected and quantified. The collection of air samples for the analysis of trace-level constituents, however, demands highly skillful approaches relative to ones contained in other environmental media. This is especially the case, when highly reactive, or unstable, gaseous components like volatile organic compounds (hereafter VOC) are concerned [1,2]; with their short lifetimes on the order of a few days, various VOC are known to contribute to the formation of photochemical ozone [3]. Accurate quantification of ambient VOC concentration data is hence considered to be a principal task in resolving atmospheric pollution problems associated with airborne ozone [4].

The collection of airborne VOC is normally performed either by directly filling air samples into different container types (canister or Tedlar bag) or by indirectly transferring target analytes onto less voluminous, sorptive materials [5,6]. Samples are typically analyzed by being introduced into the GC detection line via various combinations of (cyro-) focusing or thermal desorption stages (e.g., [7]). Because of complexities involved in such pre-concentration procedures, some authors have put enormous efforts into reducing all the errors arising from the different analytical steps.

In fact, according to many inter-comparative studies conducted with the aim of gaining high-quality analytical data, fairly excellent agreements in the measurement data are commonly observed among different research groups (e.g., [8]). A close inspection of those experimental data generally

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* Corresponding author. Tel.: +82-2-3408-3233; fax: +82-2-499-2354.
E-mail address: khkim@sejong.ac.kr (K.-H. Kim).

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suggests that sufficient effort was directed to the improvement of QA/QC procedures at various quantification stages. This finding thus contrasts sharply with the lack of studies devoted to the elimination or minimization of errors inherent in the collection stage of air samples, which can be as significant as those errors involved in the analytical steps [9].

For the purpose of establishing a reliable sampling method for airborne pollutants, we investigated in this study the analytical performance of three different sampling methods that basically rely on the combination of the sorptive sampling technique and the regulation of the sampling flow by MFC. Through an application of these different sampling approaches on the analysis of several major aromatic VOC in ambient air, we attempted to evaluate the sampling-related bias from various respects. Considering the aim of our present investigation, the results of our study will be used to estimate and to address sampling uncertainties that were unaccounted for by most previous studies.

2. Materials and methods

2.1. Three independent instrumental systems for collecting VOC samples

In this study, three different sampling methods were compared and examined for the collection and analysis of major aromatic VOCs, including benzene, toluene, ethylbenzene, and xylenes (commonly called, BTEX) in ambient air. The main basis of our present study is to produce the most reliable data sets by operating our replicate measurement system, i.e., a six-port manifold mass flow controller (MFC) system. Comparative data sets for BTEX are then also obtained by the two other sampling techniques to evaluate the compatibility of different sampling techniques.

For the purpose of our study, we first designed and developed an atmospheric sampling system (for ambient VOC) that utilizes a single vacuum pump connected via a manifold to six separate mass flow controllers (MFC). This system will be referred to as the Sejong University MFC (SJU-MFC) system. The configuration of this system was first introduced to achieve precise control of air-sampling volumes for the accurate quantification of vertical concentration gradients of Hg (for the schematic of this system, refer to Kim and Lindberg [10]). The vacuum manifold of our SJU-MFC system is controlled by a small vacuum pump (GAST). The individual MFC units for this system are KOFLOC model 3660A (Japan) with a variable flow capacity from 20 to 1000 ml min^{-1}. The performance criteria of this MFC system were tested in terms of: (1) flow rate; (2) MFC-MFC variability; (3) (sampling) tube-tube variability; and (4) time. It was interesting to find that the latter two factors did not show any significant variations, while the former two show substantially large variations. For instance, to specify the effects of these variables, their reproducibilities were compared in terms of relative standard error (R.S.E.); it was found that MFC-MFC variability was generally found in a few tens of per cent value, while that of tube-tube variability on the order of a few per cent. Knowing that MFC bias is affected most sensitively as a function of flow rate, we computed and used correction factors for each MFC unit at varying flow rates (such as 20, 40, 100, 200, 300, 400, 500, and 1000 ml min^{-1}) by following the procedures of Kim and Lindberg [10]. It was found that bias values tend to decrease systematically with an increasing flow rate. However, as most of those variabilities are constant enough to maintain highly systematic patterns, we were able to characterize all those MFC biases at a given flow rate.

In analogue to the SJU-MFC system, two different sampling techniques, including both an automatic continuous sampler (ACS) and an on-line GC (O-GC) analyzer, were employed in our comparative VOC measurements. The former, the ACS system is a Sentry II model of Bios Co. (USA) and built to collect up to 24 individual adsorption tubes. The ACS system can control flow rates in the range of 1–200 ml min^{-1}. For the purpose of our comparative study, two replicate samples were collected for each set of comparative analysis using the ACS. By contrast, the O-GC system is made up of both the thermal desorption unit (TDU) of UNITY model (Markes, UK) and the GC-FID system (DS 6200 model, Donam Instruments, Korea). Unlike the other systems described above, the O-GC system is a full set of instruments combining the functions of both sampler and analyzer to allow continuous measurements of BTEX. Hence, this O-GC system is distinguished from the other two systems in that it does not require additional manual treatment of collected samples for the measurements of BTEX analytes. Although flow rates of ACS and O-GC system are also regulated by MFC, they are not flexible enough to collect samples at a wide range of flow rates (relative to SJU-MFC system). Hence, unlike the case of our SJU-MFC system, their flow rate biases were tested mainly at the actual field sampling flow rate (e.g., 40 ml min^{-1}). Flow rates for all sampling systems were corrected by a digital flow meter (DC-1 Flow Calibrator, BIOS Inc.) under the field conditions.

In the course of our study, all comparative experiments were made simultaneously by two or three different sampling methods described above. The concentrations of BTEX were then determined by an identical GC-FID system such that those samples collected by two off-line sampling systems (SJU-MFC and ACS) were analyzed in the off-line mode of the O-GC system right after the acquisition of BTEX data set on the on-line mode. In addition, the use of the two off-line sampling systems can be distinguished from the on-line sampling system in the manner how the initial collection of BTEX samples is made. In the case of the former type, external adsorption tubes (described below) are a prerequisite for sampling and subject to thermal desorption to transfer the analytes into a cryo-focusing cold trap installed internally in the TDU. However, such procedures are omitted in the latter type, as the analytes are

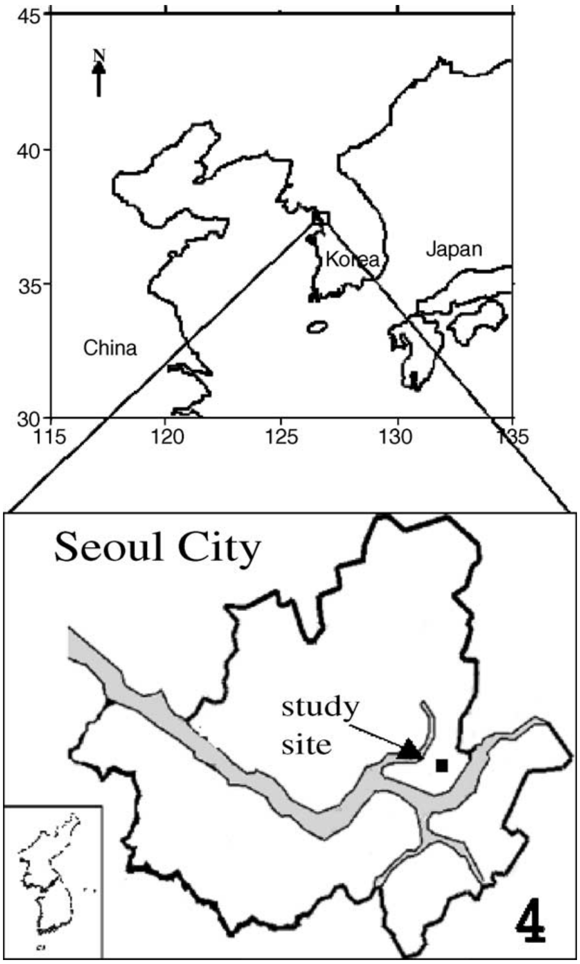

Fig. 1. A geographical location of Seoul metropolitan area in Korea and of the study site.

collected directly by the cold trap with an aid of air server system.

2.2. The collection of air samples

In the present study, samples for the analysis of ambient BTEX levels were collected from the outdoor air in the atmospheric environment laboratory at Sejong University (Seoul, Korea); the laboratory is located on the fourth floor of the six story Natural Science Building at Sejong University in Seoul, Korea (Fig. 1). The measurements of BTEX concentrations were normally made one to two times each day during a 14 day period (covering 9–23 October 2002) by running the three different aforementioned systems.

The sample collection tubes, used by both SJU-MFC and ACS system in this study, were designed using a stainless steel tube (9 cm length and 6.3 mm o.d.) packed with two different types of adsorbents in a 2:1 ratio of Carbopack C^{TM} (60/80 meshes: ∼0.4 g) and Carbopack B^{TM} (60/80 meshes: ∼0.2 g). The former with low density (∼10 m^2 g^{-1}) is a moderately weak adsorbent for collecting heavy VOC with C_8–C_{20}, while the latter with high density (∼100 m^2 g^{-1}) is considered to be the optimal choice for the low- to medium-weight range of VOC with C_4–C_8. These sampling tubes (or traps) were conditioned for 1 h at 350 °C with a constant supply of N_2 at 50 ml min^{-1}. They were then stored after being sealed by both Swagelok fitting and PTFE ferrules.

The collection of each sample by both SJU-MFC and ACS system was made with an hourly duration at flow rates of 20–30 ml min^{-1}. On the other hand, that for O-GC was made with a slightly shorter duration of 45 min for the allowance of additional steps for a full hourly on-line operation cycle. Samples collected on the adsorption tubes (by the two former method) were interfaced with the combination of an automatic TDU and the laboratory GC-FID system and analyzed in the following sequence: (1) initial thermal desorption of a sample tube at 350 °C for 5 min; (2) focusing of BTEX on cold trap at −15 °C; (3) secondary thermal desorption at 300 °C for 5 min; and (4) subsequent delivery of BTEX into the GC system. The cold trap used in the focusing stage was prepared by packing two adsorbents described above in the same manner as that for the sample collection tube. Those transported BTEX were then separated on BP-1 column (0.32 mm × 60 m, 1 μm) and detected by the FID detector.

The breakthrough volume for the adsorption system, when checked by applying standards into two sample tubes in a row, did not show any notable signal of overload up to our upper-bound test range of 500 ppb concentration levels. The precision of the analytical system was estimated by evaluating the R.S.E. value of six replicate samples collected by our SJU-MFC system. The precision of BTEX, if quantified individually for each specie at known quantities, varied among species but was generally in a few per cent range (2.7–9%); details are discussed below. 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 (within a few per cent range in general) in BTEX concentration levels between two standard types. The detection limit of those aromatic VOCs was commonly achieved at 0.1 ng level of C.

3. Results and discussion

3.1. Results of VOC determination by SJU-MFC system

In this study, the concentrations of BTEX compounds were measured concurrently with an aid of three different sampling methods for the period covering 9–23 October 2002. In the course of our study, a total of 10 comparative experiments were conducted mostly in the late afternoon or in the early evening period between 13:00 and 21:00 h. A statistical summary of the major environmental parameters

Table 1
A statistical summary of meteorological parameters measured during the whole study period (9–31 October 2002)

	Temperature (°C)	UV ($MJ\,m^{-2}$)	RH (%)	Windspeed ($m\,s^{-1}$)
Mean	13.2	12.9	58.0	0.40
S.D.	6.09	5.81	19.6	0.55
Min.	0.20	0.20	15.0	0.00
Max.	27.8	27.2	97.0	3.60
Cl (90%)	0.44	0.42	1.42	0.04

RH: Relative humidity; $N = 517$.

monitored concurrently is also provided in Table 1. As seen in Table 1, the study site was affected by highly variable temperature change during this fall season with the mean temperature of 13 °C. In addition, winds were dominantly rising from west and occasionally from east. The results of BTEX measurements made by our SJU-MFC system are also presented as both individual data sets (Table 2) and as a statistical summary (Table 3). According to the summary shown in Table 3, the highest concentration of 18.8 ± 9.3 ppb is seen for toluene, but the lowest of 0.70 ± 0.47 ppb for *o*-xylene. On the other hand, most other aromatic VOCs measured in this study were generally seen at mean concentrations around 1 ppb. Hence, except for the case of toluene with notably high concentration, the observed concentration levels in the study area appear to be comparable to those typically reported in other urban areas in Korea (e.g., [11]). However, the abnormal behavior of toluene is found not only by its largest concentration of all investigated species but also by its relative relationships with others; for instance, under many circumstances, the toluene to benzene ratio in ambient air generally fell in the range of 2–3 (e.g., [12]). The presence of the abnormally high toluene levels in this study site may have to be attributed to the strong anthropogenic source processes in the nearby Sung Soo (SS) district, 2 km to the west of our study area. Although detailed information of such source processes is yet unrevealed and unavailable, the SS district has been characterized by high toluene values; it is well known for a multitude of small-scale urban plants and industrial activities [13].

In Fig. 2, the results of up to six replicate analyses are plotted for each individual BTEX component as a function of time. According to this analysis, most compounds tend to exhibit similar distribution patterns so that their maximum and minimum concentrations occur quite consistently. To describe the compatibility of their temporal distribution patterns, we examined the relative amplitude (RA) of the temporal variability, using our BTEX data collected by the SJU-MFC system as follows:

$$\text{Relative amplitude, RA : (\%)} = \frac{\text{Max.} - \text{Min.}}{\text{Mean}} \times 100$$

The results of this analysis show that the computed RA values increase in the following order: 117 (benzene), 132 (toluene), 160 (ethylbenzene), 205 (*o*-xylene), and 234%

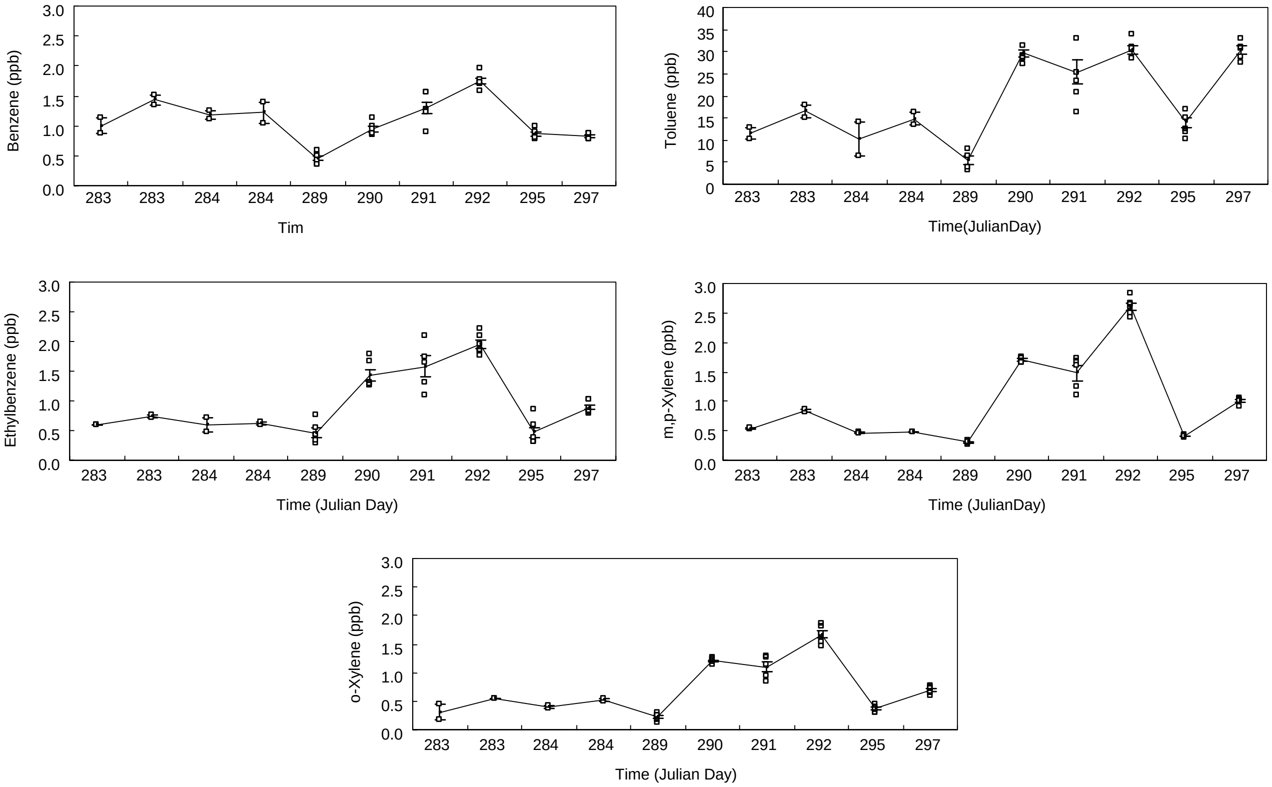

Fig. 2. Results of BTEX measurement data obtained by a six-port MFC system during the entire study period (9–23 October 2002). (Julian day 282 corresponds to 9 October 2002).

Table 2
Replicate measurements of BTEX (up to six replicate samples) were made by running a six port MFC sampling system (so called as SJU-MFC) described in the text

Exp no.	Time	Julian day	Channel						Mean	*N*	S.D.	S.E.	R.S.E.
			1	2	3	4	5	6					
Benzene													
1	20	282.8	0.88	1.13					1.00	2	0.18	0.13	
2	21	282.9	1.34	1.52					1.43	2	0.12	0.09	
3	12	283.5	1.26	1.12					1.19	2	0.10	0.07	
4	13	283.6	1.04	1.41					1.22	2	0.26	0.18	
5	14	288.6	0.35	0.53	0.60	0.50	0.42	0.36	0.46	6	0.10	0.04	8.80
6	14	289.6	1.14	0.84	0.85	0.87	0.99	0.96	0.94	6	0.12	0.05	5.01
7	16	290.7	1.28	1.56	1.26	1.56	0.90	1.22	1.30	6	0.25	0.10	7.80
8	14	291.6	1.77	1.97	1.71	1.72	1.59	1.72	1.75	6	0.12	0.05	2.89
9	13	294.5	0.88	1.32*	0.89	0.98	0.78	0.81	0.87	5	0.08	0.03	3.98
10	15	296.6	0.77	0.87	0.79	0.78	0.54*	0.87	0.82	5	0.05	0.02	2.77
Toluene													
1	20	282.8	10.1	12.9					11.5	2	1.93	1.37	
2	21	282.9	15.1	17.9					16.5	2	1.99	1.41	
3	12	283.5	6.38	14.2					10.3	2	5.53	3.91	
4	13	283.5	13.5	16.3					14.9	2	1.96	1.38	
5	14	288.6	3.18	3.75	6.38	7.98	3.96	7.89	5.52	6	2.17	0.88	16.0
6	14	289.6	29.1	28.3	27.3	28.6	31.3	33.2	29.6	6	2.18	0.89	3.00
7	16	290.7	23.4	25.3	20.9	33.0	16.3	33.0	25.3	6	6.67	2.72	10.7
8	14	291.6	30.3	34.0	31.1	28.4	30.7	27.1	30.3	6	2.38	0.97	3.21
9	13	294.5	10.3	17.1	12.0	12.4	15.1	16.9	14.0	6	2.81	1.15	8.20
10	15	296.6	27.5	31.2	28.7	30.6	33.0	31.3	30.4	6	1.97	0.80	2.65
Ethylbenzene													
1	20	282.8	0.60	0.60					0.60	2	0.00	0.00	
2	21	282.9	0.71	0.76					0.74	2	0.04	0.03	
3	12	283.5	0.48	0.72					0.60	2	0.17	0.12	
4	13	283.5	0.59	0.64					0.62	2	0.03	0.02	
5	14	288.6	0.77	0.55	0.28	0.33	0.42	0.43	0.46	6	0.18	0.07	15.7
6	14	289.6	1.77	1.66	1.27	1.32	1.26	1.28	1.43	6	0.23	0.09	6.58
7	16	290.7	2.10	1.64	1.31	1.74	1.11	4.10*	1.58	5	0.39	0.17	10.9
8	14	291.6	1.96	1.87	2.10	2.23	1.77	1.84	1.96	6	0.17	0.07	3.64
9	13	294.5	0.34	0.38	0.60	0.86	0.31	0.31	0.47	6	0.22	0.09	19.3
10	15	296.6	0.78	0.88	1.02	1.03	0.83	0.80	0.89	6	0.11	0.04	5.02
m,*p*-Xylene													
1	20	282.8	0.53	0.54					0.54	2	0.01	0.00	
2	21	282.9	0.81	0.86					0.84	2	0.03	0.02	
3	12	283.5	0.48	0.45					0.46	2	0.02	0.01	
4	13	283.5	0.48	0.48					0.48	2	0.00	0.00	
5	14	288.6	0.34	0.34	0.26	0.28	0.31	0.30	0.31	6	0.03	0.01	4.23
6	14	289.6	1.73	1.72	1.68	1.76	1.66	1.64	1.70	6	0.05	0.02	1.09
7	16	290.7	1.68	1.62	1.26	1.73	1.11	5.30*	1.48	5	0.28	0.12	8.37
8	14	291.6	2.82	2.63	2.50	2.67	2.44	2.58	2.61	6	0.13	0.05	2.10
9	13	294.5	0.43	0.44	0.37	0.40	0.40	0.41	0.41	6	0.02	0.01	2.28
10	15	296.6	0.91	1.02	1.03	1.07	1.01	1.01	1.01	6	0.05	0.02	2.20
o-Xylene													
1	20	282.8	0.44	0.17					0.30	2	0.19	0.13	
2	21	282.9	0.56	0.55					0.55	2	0.01	0.00	
3	12	283.5	0.37	0.42					0.40	2	0.03	0.02	
4	13	283.5	0.49	0.54					0.51	2	0.03	0.02	
5	14	288.6	0.30	0.24	0.13	0.17	0.26	0.25	0.22	6	0.06	0.03	11.4
6	14	289.6	1.27	1.24	1.17	1.21	1.14	1.20	1.20	6	0.05	0.02	1.62
7	16	290.7	1.27	1.14	0.94	1.30	0.84	2.08*	1.10	5	0.20	0.09	8.16
8	14	291.6	1.85	1.65	1.67	1.81	1.47	1.53	1.66	6	0.15	0.06	3.66
9	13	294.5	0.31	0.39	0.45	0.40	0.35	0.30	0.37	6	0.06	0.02	6.71
10	15	296.6	0.60	0.68	0.77	0.64	0.74	0.72	0.69	6	0.07	0.03	3.88

*The numeric data (shown in this table) can be statistically determined as outliers: they were deleted prior to the actual treatment of data interpretation.

Table 3
A statistical summary of BTEX concentration (in ppb) determined using the SJU-MFC system

	BEN[a]	TOL	EB	MPX	OX
Mean	1.10	18.8	0.93	0.98	0.70
Median	1.10	15.7	0.68	0.69	0.53
S.D.	0.36	9.3	0.53	0.74	0.47
Min.	0.46	5.52	0.46	0.31	0.22
Max.	1.75	30.4	1.96	2.61	1.66
Cl (90%)	0.21	5.37	0.31	0.43	0.27

A total of 10 measurements were made during the whole study period ($N = 10$).

[a] Acronyms of BEN, TOL, EB, MPX, and OX denote benzene, toluene, ethylbenzene, *m*,*p*-xylene, and *o*-xylene, respectively.

(*m*,*p*-xylene). The presence of large RA values or strong temporal variations appears to come mainly from the fact that the concentration levels of most compounds hiked during the three-day period of 17 through 19 October (See Fig. 2). Acknowledging the fact that such phenomenon tends to be more significant with an increase in molecular weights, it may be possible to infer that source processes of heavier compounds (e.g., xylene) may be more dynamic than those of lighter ones. However, more comprehensive studies may be needed to confirm such a possibility and the associated causes.

In light of the fact that our SJU-MFC system allows up to six replicate analyses at one time, we used those replicate data to assess MFC-MFC bias. In Table 2, relative standard error (R.S.E.) values of each compound are computed and compared for each individual experiment. In this analysis, we used the results with six replicate analyses after statistical sorting of outlier (OL); OLs were eliminated statistically using the methods of Skoog et al. [14]. However, if the occurrence patterns of OL are examined, two different types emerge in our measurement data obtained by SJU-MFC. First of all, the existence of highly consistent trend can be found in the data groups of ethylbenzene and all xylenes; all of these OLs occurred at the sixth channel in the seventh experiment. If one considers that tube-tube bias is insignificant in our SJU-MFC system, it is suspected that these outlying data were due to the moderate changes in its operation conditions. Although such results are consistent in some sense, it was not systematic enough to persist across different experiments. On the other hand, two OLs in the benzene data appear to be easily distinguishable from the other case in that they occur in a highly randomized manner. Because statistical sorting of outliers can be employed, our replicate sampling system can be useful enough to obtain data sets of high statistical significance. As a means to evaluate the compatibility or reproducibility of data, we computed relative standard error (R.S.E. = S.E. × 100/Mean) values of each compound for each individual experiment covering Nos. 5–10. For each compound, the mean R.S.E. value was derived after deleting both maximum and minimum R.S.E. values as follows: 3.4% (*m*,*p*-xylene), 5.2% (benzene), 5.9% (*o*-xylene), 7.3% (toluene), and 10.2% (ethylbenzene). It is interesting to note that unlike the results of the largest RA value, *m*,*p*-xylene shows, the smallest R.S.E. value of all compounds.

3.2. Comparison of the data obtained by different sampling techniques

In the course of our present study, a total of ten independent experiments were carried out to check the compatibility of different sampling techniques. In each of those ten experiments, our SJU-MFC system was operated for the collection of VOC samples. However, simultaneous operation of the ACS and O-GC systems were limited to only five and eight times, respectively (Table 4). In Fig. 3, the results derived by all three different techniques are plotted as a function of time. A quick glance over the results indicates that the concentration data of all three methods in general show good similarities in both absolute and relative senses. However, if we compare the results obtained by those two systems to those made by the SJU-MFC system, the patterns are slightly different between the ACS and O-GC systems. It is seen that differences in BTEX concentrations are irregular between the ACS and SJU-MFC pair, while the results of the O-GC system tend to be slightly larger than those of the SJU-MFC system. The latter pattern became more evident during the period when high concentrations were observed.

As a means to evaluate the differences among different sampling systems, we computed the per cent difference (PD) values of the two different types as follows:

$$\mathrm{PD_1}(\%) = \frac{\text{SJU-MFC} - \text{ACS}}{\text{SJU-MFC}} \times 100 \qquad \text{(A)}$$

$$\mathrm{PD_2}(\%) = \frac{\text{SJU-MFC} - \text{O-GC}}{\text{SJU-MFC}} \times 100 \qquad \text{(B)}$$

If the PD values derived by formula (A) are compared between different compounds, the patterns are highly diverse. In the case of benzene, the ACS generally exhibited larger values than the SJU-MFC system with a mean PD value of −26.5%. However, the patterns were reversed for both ethylbenzene (20.5%) and toluene (34.4%). The results of the paired t-test indicated that these differences between two different methods are significant statistically at 95% confidence level. However, no such distinctions were evident for any compounds other than those three. On the other hand, the results derived by formula (B) showed PD values in the range of −17% of ethylbenzene to +2.5% of toluene. It was found for a few compounds (e.g., toluene and all xylenes) that the concentrations derived by the O-GC system tend to be larger than those of the SJU-MFC system. The findings of relatively enhanced values in the former are suspected to be caused by its improved recovery since it involves less sample handling procedures than those of the latter (as discussed above). However, differences between the two systems were in all cases statistically insignificant (at 95% confidence interval). Consequently, it may be concluded that the BTEX

Table 4
The BTEX concentration data obtained by a six-port SJU-MFC system are compared against those obtained by the two other sampling systems

Experiment	SJU-MFC					Automatic continuous sampler (ACS)					Per cent difference (%)[a]				
no. ($N = 5$)	BEN[b]	TOL	EB	MPX	OX	BEN	TOL	EB	MPX	OX	BEN	TOL	EB	MPX	OX
(A) SJU-MFC vs. automatic continuous sampler (ACS)															
1	1.00	11.5	0.60	0.54	0.30	1.44	9.91	0.43	0.50	0.70	−44.0	13.8	28.3	6.93	−132
2	1.43	16.5	0.74	0.84	0.55	1.73	10.5	0.54	0.77	0.74	−20.8	36.5	26.2	7.46	−33.8
3	1.19	10.3	0.60	0.46	0.40	1.25	5.58	0.43	0.47	0.38	−4.85	45.8	28.8	−1.16	3.57
4	1.22	14.9	0.62	0.48	0.51	1.69	6.31	0.55	0.59	0.41	−38.2	57.6	11.8	−22.7	20.5
5	0.46	5.52	0.46	0.31	0.22	0.60	6.21	0.45	0.31	0.12	−30.8	−12.5	1.97	−1.26	46.3
Mean	1.06	11.74	0.60	0.52	0.40	1.34	7.70	0.48	0.53	0.47	−26.5	34.4	20.5	−0.7	−18.3
Experiment	SJU-MFC					On-line GC (O-GC)					Per cent difference (%)[c]				
no. ($N = 8$)	BEN	TOL	EB	MPX	OX	BEN	TOL	EB	MPX	OX	BEN	TOL	EB	MPX	OX
(B) SJU-MFC vs. on-line GC (O-GC) System															
3	1.19	10.3	0.60	0.46	0.40	0.98	8.75	0.61	0.50	0.48	17.5	15.0	−2.50	−8.10	−22.0
4	1.22	14.9	0.62	0.48	0.51	0.97	9.67	0.64	0.60	0.57	20.6	35.0	−3.98	−25.5	−11.4
5	0.46	5.52	0.46	0.31	0.22	0.61	5.76	0.38	0.42	0.35	−32.5	−4.33	17.6	−37.9	−54.1
6	0.94	29.6	1.43	1.70	1.20	1.28	35.6	1.43	1.76	1.17	−36.4	−20.1	−0.17	−3.47	2.97
7	1.30	25.3	1.58	1.48	1.10	1.41	26.8	1.67	1.53	1.10	−9.13	−5.77	−6.06	−3.36	−0.38
8	1.75	30.3	1.96	2.61	1.66	1.87	35.6	2.59	3.52	2.20	−6.87	−17.6	−32.4	−35.0	−32.1
9	0.87	14.0	0.47	0.41	0.37	1.05	8.72	0.65	0.55	0.39	−21.1	37.6	−40.1	−34.0	−5.05
10	0.82	30.4	0.89	1.01	0.69	0.90	19.6	1.05	0.98	0.67	−10.1	35.4	−18.3	3.16	2.55
Mean	1.13	25.9	1.26	1.44	1.00	1.30	25.3	1.48	1.67	1.11	−14.9	2.53	−17.1	−15.7	−10.0

[a] Per cent difference (%) = (MFC−ACS)/MFC × 100.

[b] Refer to Table 3 for the full information of acronyms used in this table.

[c] Per cent difference (%) = (MFC−O-GC)/MFC × 100.

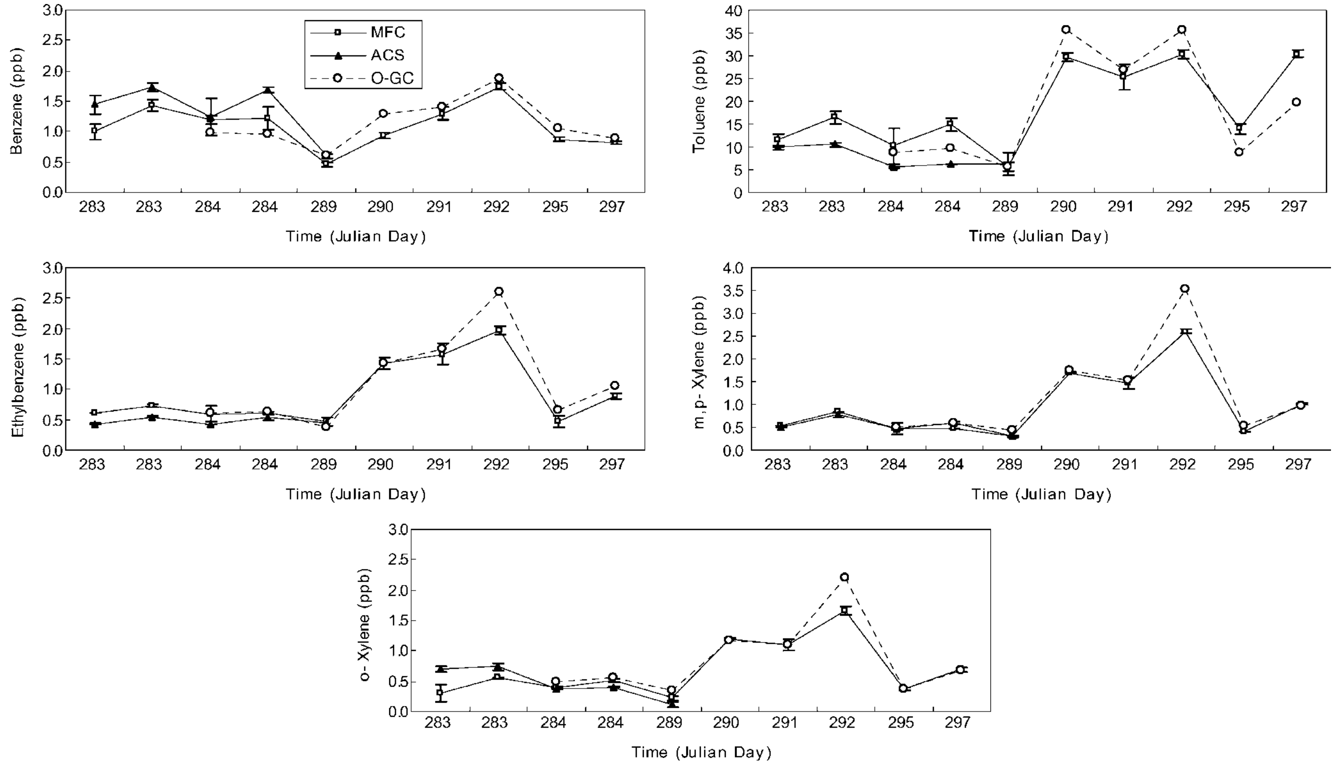

Fig. 3. Comparison of temporal variabilities of BTEX compounds measured during the whole study period in October 2002.

concentration data derived by the SJU-MFC and O-GC systems are in most cases in good agreement.

To further analyze the relationships between different sampling methodologies, we conducted a correlation analysis of concentration data sets obtained by different sampling methods (Fig. 4). The existence of strong correlations between the SJU-MFC and ACS systems is evident for the concentration data sets of a few species (e.g., benzene and *m*,*p*-xylene). By contrast, the results between the SJU-MFC and O-GC systems are much more improved, as all matching pairs are found to exhibit excellent correlations ($P \leq 0.005$). The results of our correlation analysis hence appear to be quite compatible with those derived by comparing absolute differences as PD values. Consequently, the overall results of our comparison, conducted to test the compatibility among different sampling methods, consistently indicate that the O-GC system exhibits more enhanced agreement with the SJU-MFC system than the ACS system in both absolute and relative senses. The relative lack of compatibility found in the ACS system may be accounted for by a number of factors. Most importantly, as the ACS allows a single (or double) sampling at each sampling, screening of OL is not limited (relative to SJU-MFC). In addition, as the samples collected by ACS needs additional sample handling for GC analysis (relative to O-GC), it is more liable to errors than the O-GC system.

Although this study was primarily intended to test the compatibility of different sampling methods, our data can be used to provide some insights into the factors affecting the BTEX behavior under the environmental conditions of our study. For this purpose, we conducted a correlation analysis not only between different compounds but also between BTEX and other parameters (Table 5). The results of this analysis generally indicate the common occurrences

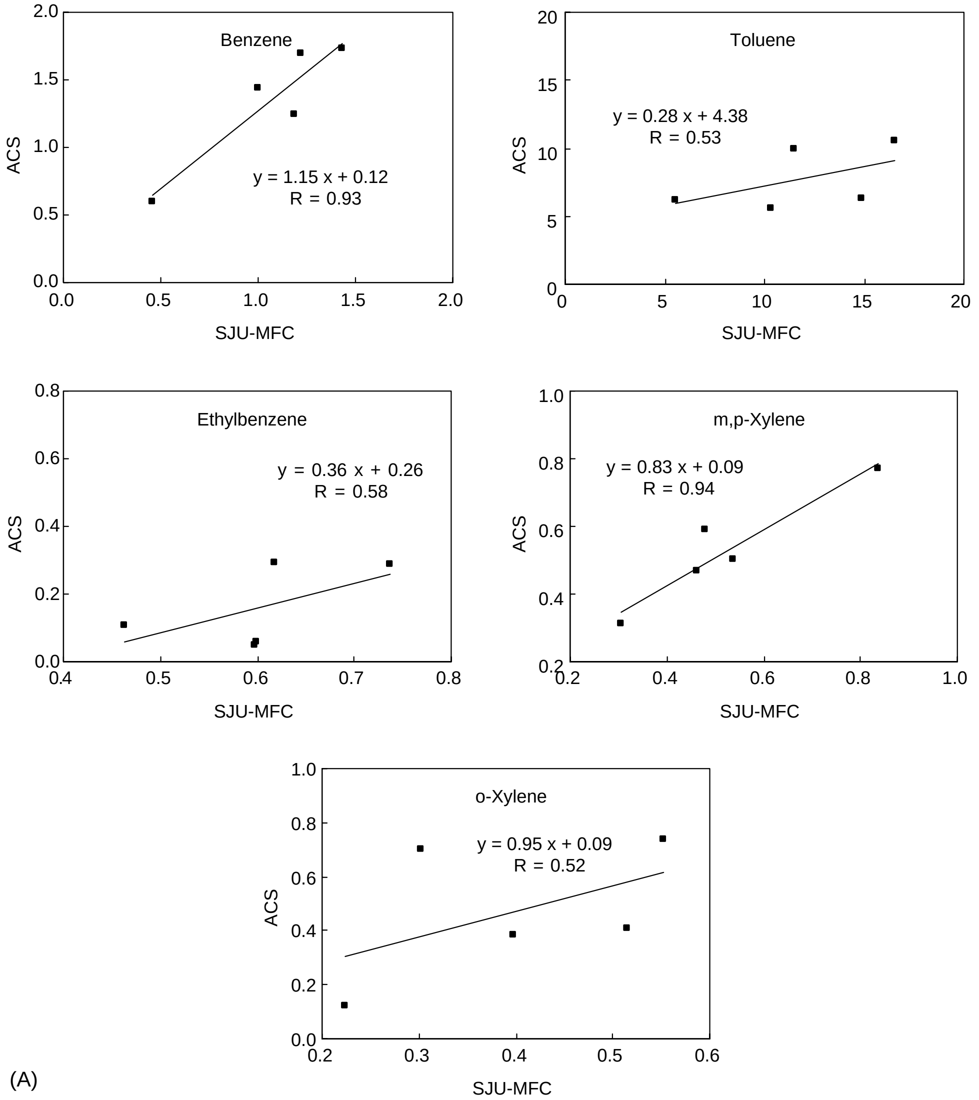

Fig. 4. Plot of linear regression analysis of BTEX concentration data obtained by different sampling methods. (A) SJU-MFC vs. automatic continuous sampler (ACS) system, and (B) SJU-MFC system vs. on-line GC (O-GC) system.

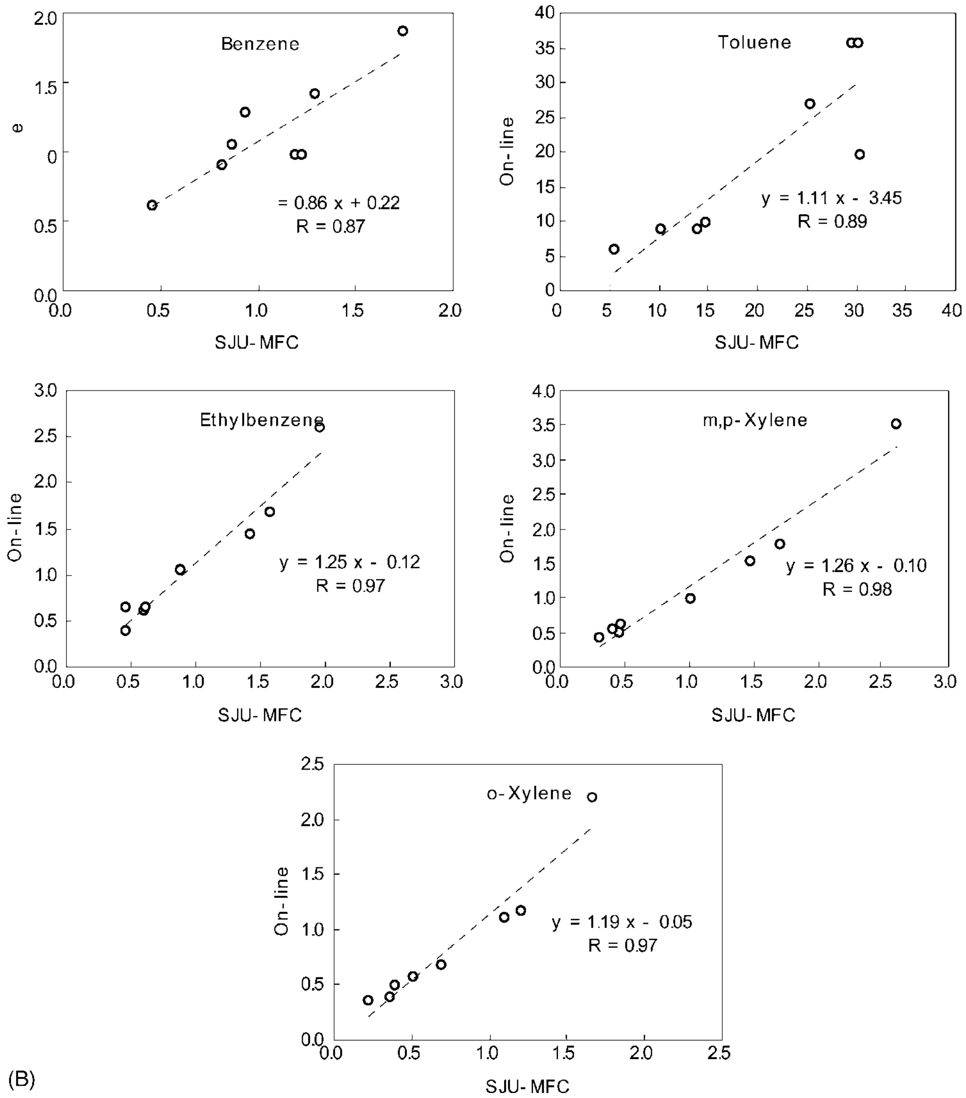

Fig. 4. (*Continued*).

Table 5
Results of correlation analysis between BTEX and relevant environmental parameters

	BEN[a]	TOL	EB	MPX	OX
BEN	1				
TOL	0.29	1			
EB	0.52*	0.88*	1		
MPX	0.57*	0.84*	0.98*	1	
OX	0.56*	0.86*	0.99*	0.99*	1
TEMP	0.43	−0.06	0.34	0.28	0.31
UV	0.51*	0.07	0.46	0.40	0.43
RH	0.05	−0.19	−0.10	−0.03	−0.05
WS	−0.13	0.49	0.30	0.20	0.23

Asterisk denotes the probability of no correlation <0.01.

[a] Refer to Table 3 for the full information of acronyms used in this Table.

of excellent correlations among the chemicals, while strong correlations are almost absent between BTEX and meteorological conditions. Such patterns of correlation analysis were in fact observed in a number of previous studies (e.g., [13]). As such, it is difficult to expect the direct influence of physical conditions on BTEX concentration levels. It should however be noted that the behavior of benzene is distinguished from others, as all the other VOC exhibit excellent inter-compound relationships with r values of 0.84–0.99. In addition, the results of benzene are further distinguished from others, such as its relationship with meteorological parameters. Unlike other compounds, benzene alone shows a good correlation with irradiance data ($r = 0.51$, $N = 11$, $P < 0.05$). This type of uniqueness in the environmental behavior of benzene (among different aromatic VOC) has in fact been reported by a number of studies describing BTEX behavior in landfill environment [15] and indoor atmospheres [16]. However, the results of Tran et al. [17] reported a highly contrasting pattern wherein all BTEX exhibit good correlations with each other. These results thus suggest that the patterns of BTEX behavior can differ between different studies. However, such differences, if existing, can arise mainly from benzene's relationship with other aromatics.

4. Summary

In the course of the present study, we examined the compatibility of different sampling approaches by the concurrent analysis of the BTEX concentration data obtained by three techniques, which include (1) a six-port manifold MFC system (SJU-MFC), (2) an automatic continuous sampler (ACS), and (3) an on-line system allowing automatic sampling and GC detection methods (O-GC). To make a meaningful comparison of our measurement data, we initially inspected our replicate data sets determined by the SJU-MFC system. The compatibility of this SJU-MFC system was then checked carefully against the results of the other two methods. The results of all the different data sets obtained by different methods were compared by a number of approaches. According to the results of our analysis, the data sets obtained by all three sampling methods were generally compatible enough. However, they also differ slightly in both absolute and relative terms. It was found that the absolute differences between the ACS and SJU-MFC systems were irregular, while those determined by the O-GC showed slight enhancement relative to the SJU-MFC. If the correlations of BTEX compounds were used to examine the compatibility of different systems, the results derived by the latter pair were found to be excellent in most compounds. On the other hand, the patterns of the former pair were rather selective to show good correlations depending on the compound.

The results of our study demonstrate that high-quality BTEX data can be obtained by our multi-channel sampling system called as the SJU-MFC system because it allows the statistical sorting of the unusual concentration data. The reliability of the other sampling methods were hence tested and compared against the SJU-MFC system. It is found that absolute and relative relationships between different sampling systems can vary in a moderately different manner. Although the performance of a commercial ACS system appeared to be less reliable than the other two, the agreement among different sampling techniques is found to be reasonably good enough. As observed in this study, constant evaluation of each sampling system can be a basic requirement to verify and maintain the quality of the measurement data.

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