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Assessment of VOCs emission inventory in Seoul through spatiotemporal observations using passive and online PAMS measurements

Jimin Lee[a], Meehye Lee[b], Limseok Chang[c], Sun-A Shin[c], Kwangrae Kim[d], Yongsuk Choi[d], Hakmyeong Lim[d], Sung-Deuk Choi[e], Gangwoong Lee[a,*]

[a] Department of Environmental Science, Hankuk University of Foreign Studies, Yongin, South Korea
[b] Department of Earth and Environmental Sciences, Korea University, Seoul, South Korea
[c] Environmental Satellite Center, National Institute of Environment Research, Incheon, South Korea
[d] Seoul Metropolitan Government Research Institute of Public Health and Environment, Seoul, South Korea
[e] Department of Civil, Urban, Earth, and Environmental Engineering, Ulsan National Institute of Science and Technology, Ulsan, South Korea

HIGHLIGHTS

- Passive air sampling effectively mapped the spatial distribution of VOCs across Seoul.
- PMF factors reasonably matched the spatial distributions of area and road emissions.
- Notable winter increases in VOCs were observed in the industrial and commercial areas.
- Current emission inventory overestimates aromatic composition including benzene.
- The study identified an underestimation of VOCs emissions, particularly during summer.

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ABSTRACT

We have conducted a quantitative analysis of volatile organic compounds (VOCs) in Seoul from September 2022 to June 2023, employing passive air samplers (PAS) at 25 sites and continuous monitoring at five photochemical assessment monitoring stations (PAMS). Comparing VOCs concentrations and compositions from PAS and PAMS during the same time periods, we found that most VOCs showed no significant difference (p-value >0.05) between the methods, except for olefins, which were overestimated by 24 % in passive sampling, confirming PAS as an effective tool for assessing the spatial distribution of VOCs species over large areas. Throughout Seoul, median values of total volatile organic compounds (TVOCs) concentrations collected with passive samplers remained stable with a standard deviation of 1.22 ppbv, typically ranging from 11 to 13 ppbv, except for an increase during winter in the southwestern regions of the city, where intense industrial and vehicular emissions are reported in the current Clean Air Policy Support System (CAPSS) emissions inventory. Positive matrix factorization (PMF) analysis using the passive data revealed general consistency in the spatial distribution of area and road emissions when compared with CAPSS emission inventory, although localized discrepancies were observed. In quantitative assessments of TVOCs comparing PAS observations with emission-based models, modeled values were within 1.5 times the interquartile range of observed PAS concentrations over Seoul. However, the lack of detection of emission hotspots in southeastern Seoul in the PAS data, coupled with the omission of photochemical loss in our dispersion-only models, indicates that the current CAPSS emission inventory may significantly underestimate actual ambient VOCs levels, especially in summer.

1. Introduction

Volatile Organic Compounds (VOCs) are organic substances which have high vapor pressure, allowing them to readily evaporate into the atmosphere. These compounds typically exhibit a boiling point ranging from 50 to 260 °C at standard temperature and pressure. VOCs

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* Corresponding author. Department of Environmental Sciences, Hankuk University of Foreign Studies, Yongin, South Korea.
E-mail address: gwlee@hufs.ac.kr (G. Lee).

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encompass a diverse range of compounds, including aromatic and aliphatic hydrocarbons, aldehydes, ketones, and halogenated hydrocarbons, each distinguished by their molecular structure and composition (Demirel et al., 2014; Solomon et al., 2007). These compounds are emitted from various anthropogenic activities, such as the combustion of fossil fuels, industrial processes, and the use of organic solvents in everyday life (Muller, 1992). Additionally, natural sources, such as various vegetations, contribute to VOCs emissions, referred to as Biogenic Volatile Organic Compounds (BVOCs) (Dumanoglu et al., 2014; Guenther et al., 2006; Tie et al., 2006).

VOCs serve as precursors in the formation of secondary pollutants, including ozone (O_3), secondary organic aerosols (SOA), and peroxyacyl nitrates (PAN), through photochemical oxidation reactions in the troposphere. Ozone, in particular, poses significant health risks, affecting human health and vegetation, especially in densely populated urban areas (Hidy, 2000; Kleinman et al., 2000). In addition to their role as precursors to air pollutants, some VOCs, such as benzene, ethylbenzene, and halogenated VOCs, are recognized as carcinogens and hazardous substances (Cakmak et al., 2014; CEPA, 1999; IARC, 2013; Woodruff et al., 1998). While all VOCs, particularly halogenated ones, are infrared active, their reaction products, such as organic aerosol and ozone, can also affect climate forcing directly by reflecting or absorbing light, and indirectly by modifying cloud albedo and lifetime (Ebi and McGregor, 2008; Ramanathan and Crutzen, 2003; Western et al., 2024). Consequently, VOCs have significant direct and indirect impacts on human health and climate change (Bozkurt et al., 2018; Rosenfeld et al., 2014).

Seoul, South Korea's capital, though geographically compact with an area of 605 square kilometers, hosts a dense population of approximately 9.5 million people, alongside significant commercial and domestic activities. Seoul has experienced a concerning trend of increasing ozone concentrations, necessitating urgent policy interventions (Kim et al., 2021a). Recent observations in Seoul have identified high concentrations of VOCs, notably ethane, propylene, n-butane, and toluene primarily emanating from residential LNG (Liquefied Natural Gas) usage, mobile traffic sources, fossil fuels and solvent use respectively (Kang et al., 2022; Simpson et al., 2012). A study showed that toluene has accounted for about 28 % of the total ozone formation and 2.5–3.5 $\mu g\ m^{-3}$ of total SOA formation potential (Shin et al., 2013). Given Seoul's unique topography, which is surrounded by forested areas, simulation results indicate that BVOCs emissions could increase daytime ozone production by up to 20 ppbv in Seoul. (Kim et al., 2013).

Historically, the emission inventory of VOCs in Seoul has shown the highest uncertainty among the major air pollutant species (Jang et al., 2023). This uncertainty has been significantly reduced in recent years by intensive campaigns such as MAPS-Seoul (Kim and Lee, 2018), KORUS-AQ (Crawford et al., 2021), and SIJAQ (Park et al., 2024), with recent estimates placing it in the range of 13–23 % in the Seoul area (Kwon et al., 2021). The emission inventory of VOCs in Seoul has been primarily validated by aircraft and ground observations at specific times and locations (Simpson et al., 2020). However, these approaches are limited in their ability to capture the highly variable spatial characteristics of VOCs emissions in Seoul.

VOCs monitoring using passive air samplers (PAS) is particularly well suited for simultaneous, long-term, large-scale studies. For this reason, PAS has been consistently applied to spatially distributed VOCs observations (Huang et al., 2018). In Korea, PAS has mainly been used to assess the impact of emission sources in industrial areas such as Ulsan and Shihwa on the surrounding regions (Byeon et al., 2011; Park et al., 2022). In Seoul, the first investigation of VOCs concentrations using PAS with a special focus on toxic organic species (TO-15) was recently conducted by Kim et al. (2021c). Although they successfully characterized the distributions of TO-15 VOCs from a health perspective, they did not identify those of US EPA's PAMS (Photochemical Assessment Monitoring Stations) VOCs associated with aerosol and ozone production in Seoul (Kim et al., 2018a, 2021b).

Furthermore, the spatiotemporal variations of ambient VOCs were not well compared with the Clean Air Policy Support System (CAPSS) inventory data in Seoul, which hindered the adequate validation of the current VOCs inventory. The most recent emission inventory of VOCs (Choi et al., 2022) needs to be validated to account for the continuously changing behavior, such as the 26 % decrease observed in Seoul between 2007 and 2014 (Kim and Lee, 2018).

The primary objective of this study is to characterize the spatiotemporal profiles of PAMS listed VOCs species emissions in Seoul using both passive and continuous monitoring methods. In addition, this research seeks to evaluate the accuracy of the VOCs emission inventory by comparing observed spatiotemporal VOCs concentrations with simulated concentrations derived from CAPSS driven simplified models. Through this comparative analysis, we aim to improve our understanding of the reliability of VOCs data within the current VOCs inventory and consequently refine strategies for VOCs mitigation in Seoul. Ultimately, this study seeks to provide valuable insights into VOCs emissions in urban environments and to provide essential tools with PAS method for spatial assessment of VOCs in Seoul and similar metropolitan areas.

2. Method

2.1. Sampling sites

From September 2022 to June 2023, we measured VOCs following the U.S. EPA PAMS protocol using two independent sampling methods: long-term PAS and real-time online sampling (Lonneman, 1994; Nguyen et al., 2009). PAS measurements were conducted during three seasonal campaigns (September 16 to October 7, 2022; February 2 to 23, 2023; and May 25 to June 25, 2023) at 25 urban air quality monitoring stations in Seoul, South Korea (indicated by yellow squares in Fig. 1). Additionally, 1-h continuous real-time PAMS measurements were carried out at four of these sites (indicated by red squares) and one background site (indicated by blue square), operated by the Seoul Institute of Health and Environment.

2.2. Passive sampling method

PAS utilized in this investigation comprises a Supelco FLM Carbopack X (40/60 mesh) sorbent tube (89 mm in length and 6.4 mm in outer diameter) which is specifically designed for the entrapment of PAMS VOCs species (Oliver et al., 2017). Cleaning of all PAS tubes applied ultra pure nitrogen at a flow rate of 100 ml/min, maintaining temperatures within the range of 360 °C–370 °C for a duration of 3 h. Subsequently, pre-conditioned tubes were stored under refrigeration at 4–6 °C until deployment of the PAS units. Duplicate PAS units, outfitted with custom-made glass and diffusion cap to safeguard against wind variability, were co-located at sampling inlets of real-time online measurement at Air Quality Monitoring Stations, with an average elevation of 15 m. Blank levels of VOCs were determined by analyzing a series of randomly selected, pre-cleaned tubes. Throughout the duration of the study, a total of 153 samples were collected. Eight samples were discarded due to contamination identified by visible local events, such as nearby painting and construction activities. These events were documented during the installation and deinstallation phases, allowing us to determine which samples were affected by local contamination. After collection, the sample tubes were refrigerated at 1–2 °C until analysis using gas chromatography (GC) equipped with dual flame ionization detectors and thermal desorption injector.

2.3. Analytical method

PAS were subjected to analysis employing a thermal desorption system (TD, PerkinElmer TurboMatrix750) coupled with gas chromatography-flame ionization detection (GC-FID) (Table 1). Each

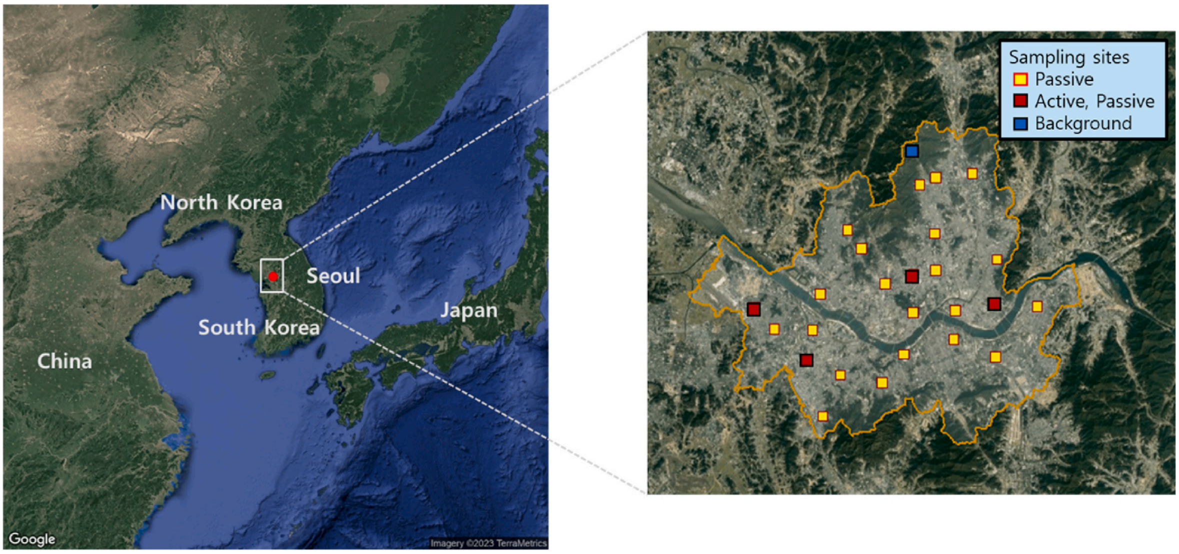

Fig. 1. Locations of passive air sampler (PAS) marked with yellow squares and continuous Photochemical Assessment Monitoring Stations (PAMS) marked with red squares in Seoul, Korea.

Table 1
Analytical conditions for measuring VOCs using PAS and online PAMS methods.

	Analytical condition	
	Online PAMS	PAS
column1	AL-PLOT: 50m × 0.32 mm × 5 μm	AL-PLOT: 50m × 0.32 mm × 5 μm
column2	BP-1 : 50m × 0.22 mm × 1.00 μm	CP-Sil 5 CB: 60m × 0.25 mm × 1.00 μm
preconcentration	−30 °C	−20 °C
initial temp	46 °C	45 °C
initial time	15 min	10 min
ramp rate	5 °C/min to 170 °C	5 °C/min to 170 °C
Isothermal hold	0 min	0 min
oven temp	15 °C/min	15 °C/min
final temp	200 °C (6 min hold)	200 °C (10 min hold)
detector	dual FID, 250 °C	dual FID, 300 °C

sample trap underwent heating to 360 °C to desorb VOCs, which were then transferred to a cold pre-concentration trap maintained at −20 °C. Subsequently, the pre-concentrated compounds were thermally desorbed at 360 °C into the GC column. The GC system utilized a Dean switch mechanism for sample injection into two distinct columns. Specifically, an AL-PLOT column (50m × 0.32 mm × 5 μm) was employed for analyzing VOCs containing 2 to 6 carbons (C_2-C_6: ethane - hexene), while a CP-Sil 5 CB column (60m × 0.25 mm × 1.00 μm) was utilized for VOCs containing 6 to 12 carbons (C_6-C_{12}: benzene - dodecane). Detection was achieved through dual flame ionization detectors (FIDs), yielding chromatographic data indicative of the detection of 52 substances out of 56 PAMS VOCs species.

For quality control of the GC system, calibration experiments for VOCs were performed using a certified PAMS VOCs standard gas mixture (RIGAS, Korea) trapped in sampling tubes. The correlation coefficients and slopes for the main species are given in the Supplement S1. The correlation coefficients (r^2) varied from 0.992 to 0.999 and the slopes ranged from 1.7 to 4.8 pA/ppbv, indicating a robust analytical method.

Real-time online analysis of VOCs at PAMS stations was conducted using a thermal desorption system (TD, PerkinElmer TurboMatrix300) coupled with online gas chromatography-flame ionization detection (GC-FID, PerkinElmer USA Clarus 500). Ambient air passed through Nafion dryer, was preconcentrated at −30 °C in a cold trap for 40 min using a TD system, followed by thermal desorption at temperatures exceeding 300 °C. The desorbed VOCs were injected into GC via high-purity N_2 gas and subsequently analyzed using dual flame ionization detectors (FID) with independent two columns (PLOT and BP-1) utilizing a Dean switch mechanism. The PLOT column was used to analyze of C_2-C_6 VOCs components, whereas a BP-1 column was employed for analyzing C_6-C_{12} components. The oven temperature was maintained at 46 °C for 15 min, then ramped to 170 °C at a rate of 5 °C/min, followed by an increase to 200 °C at a rate of 15 °C/min, where it was held for 6 min, resulting in the analysis of 56 PAMS ozone precursor VOCs over a total duration of 47.5 min.

2.4. *Precision quantification for passive samples*

Following the method of Healy et al. (2018), we calculated VOCs concentrations for the PAS using Eq-1, which incorporates parameters such as the mass of the VOCs sample (m_{meas}) in μg, uptake rate (U_{NTP}) of the VOCs at standard temperature and pressure (mL min^{-1}) listed in Supplement S2, measurement time (t) as min, mean ambient temperature during sampling (Tss) as Kelvin (Miller et al., 2022).

$$C_C = \frac{m_{meas} \times 10^6}{U_{NTP}\sqrt{\left(\frac{T_{SS}}{298}\right)}t} \tag{Eq-1}$$

Air temperature has a small effect on the determination of VOC concentrations with the passive samplers, as shown in Eq-1. The largest mean temperature difference of 20 K during our sampling period caused the maximum 3.6 % difference in concentration determination. Relative humidity has previously been shown to have a negligible effect on our Carbopack X adsorbents (Healy et al., 2021). For practical purposes, pressure correction can also be neglected. In many studies, wind speed was found to have the greatest effect on the uptake rate of a passive tube. An increase in uptake rate has been observed with increasing air velocities, typically following a logarithmic trend. Although samplers fitted with diffusion caps, as we used in this study, are more resistant to wind than open diffusion tubes, wind effects still cause uptake rate variations of 10 % (Plaisance, 2011). Therefore, the overall uncertainty of our passive sampling method due to weather conditions is estimated to be slightly over 10 %.

The method detection limit (MDL) was calculated by analyzing a 1 ppbv standard gas seven times and multiplying the standard deviation (SD) of these measurements by 3.14, as outlined in Eq-2.

$$\mathrm{MDL} = 3.14 \times \mathrm{SD} \tag{Eq-2}$$

Unlike active sampling methods for VOCs, PAS introduces inherent uncertainty and requires additional quality control measures. We sought to quantify the precision of PAS observations by collecting duplicate samples from the same location under identical conditions. The concentrations derived from these duplicate samples were compared using the following equations (Eq-3 to Eq-6) to determine the portion of the total uncertainty in the calculated concentrations.

Precision assessment included RMS (Root Mean Square) and MAD (Mean Absolute Difference) calculations based on the magnitude of the deviation between paired samples from all monitoring sites (Eq-3 and 4). Bias (Eq-5) and Percentile (Eq-6) were also calculated for VOCs concentrations greater than three times the MDL (Hyslop and White, 2009).

$$\text{RMS Precision} = \sqrt{\frac{1}{n}\sum_{i=1}^{n} D^2} \times 100\ \% \tag{Eq-3}$$

$$\mathrm{D_i} = \frac{(C_{i1} - C_{i2})/\sqrt{2}}{C_1}$$

$$\text{MAD Precision} = \sqrt{\frac{\pi}{2}}\ \frac{1}{n}\sum_{i=1}^{n} |D_i| \times 100\ \% \tag{Eq-4}$$

$$\text{Bias} = \frac{1}{n}\sum_{i=1}^{n} D_i \times 100\ \% \tag{Eq-5}$$

$$\text{Percentile Precision} = \frac{1}{2}\left(P_{84}(D_i) - P_{16}(D_i)\right) \times 100\ \% \tag{Eq-6}$$

2.5. *Positive matrix factorization (PMF) analysis*

PMF is a statistical method used mainly in air quality research, to identify and quantify the contributions of different emission sources on observed data sets (Brown et al., 2015). It models concentrations for observed species as a linear combination of distinct factors, where each factor represents an emission source. In this model framework, the selection of the ideal number of sources is crucial, as too many sources can introduce ambiguity by mixing ambiguous sources with genuine ones, while too few sources can lead to overlapping contributions. Our investigation includes four crucial metrics: Individual Mean (IM), Individual Standard Deviation (IS), Bootstrap (BS), and Displacement (DISP). IM and IS values pinpoint species that exhibit inaccuracies, with the optimal number of contaminants identified at the inflection point where these values change rapidly (Lee et al., 1999). BS simulations, performed 100 times with random seeds, ensured a stability threshold greater than 80 % for each factor. The DISP evaluation was performed when the Q-value (Q/Qexpected) stabilized or slightly decreased. Iterative analysis revealed that optimum number of emission source provided the most coherent result. This determination was supported by trends observed in IM and IS values, rapid fluctuations followed by stabilization in Q/Qexpected (Guha et al., 2015). The collective consideration of these metrics led to effectively to the segregation of distinct chemical species, thereby ensuring statistical significance.

3. Result

3.1. *QA/QC and intercomparison*

The precision estimated for the 23 VOCs detected by the 72 duplicate sample sets, which comprised a total of 144 samples from all of the PAS sites, are presented in Table 2. Precision was assessed using a variety of statistical measures: RMS precision, MAD, percentile precision, bias, and p-value. These estimates were calculated from concentrations of species that exceeded three times the MDL, which are detailed in Supplement S3. The range of values for each precision parameter across the VOCs measured is as follows: RMS Precision varied from 4.7 to 33.1 %, MAD from 4.8 to 28.4 %, Percentile Precision from 2.0 to 23.0 %, Bias ranged from −15.1 to 7.5 %, and p-values are predominantly above 0.05. Generally, the uncertainties in the duplicate VOCs samples were less than 10 %. However, for compounds with low concentrations, the uncertainty may exceed 20 %, though their impact on total VOCs was minimal due to their low concentrations. Consequently, the overall bias in the measured data was estimated to be around 10 %. This analysis highlights inherent methodological limitations and provided essential insights into the reliability and accuracy of VOCs measurements using PAS.

Table 2
Calculated RMS precisions, MAD, percentile precision, bias and p-values for selected VOCs measured by the duplicated set of PAS. (unit: % except the p-value).

Species	RMS Precision	MAD	Percentile Precision	Bias	p-value
Propylene	23.6	24.3	21.3	2.3	0.42
iso-Butane	8.3	6.4	4.6	−1.5	0.27
n-Butane	10.3	7.9	5.7	−0.5	0.68
1-Butene	26.8	26.7	21.5	−5.5	0.27
Cyclopentane	8.7	6.0	4.4	1.6	0.10
iso-Pentane	7.1	6.0	5.0	−0.7	0.41
n-Pentane	5.6	5.8	5.6	0.2	0.91
2-Methyl-pentane	6.9	7.1	4.5	4.6	0.17
Isoprene	16.8	19.3	15.3	7.5	0.48
n-Hexane	11.1	8.6	6.1	3.0	0.12
Methylcyclopentane	5.4	5.9	3.3	2.4	0.16
2,4-Dimethylpentane	5.2	5.4	3.1	1.3	0.31
Cyclohexane	11.5	11.7	11.4	−1.7	0.40
2-Methylhexane	10.9	9.4	7.1	−1.2	0.39
3-Methylhexane	33.1	28.4	21.9	−15.1	0.09
n-Heptane	4.7	4.8	2.0	3.4	0.11
Methylcyclohexane	5.7	5.5	5.5	1.7	0.44
o-Xylene	7.8	8.2	5.7	4.0	0.01
Toluene	11.2	8.3	5.7	−0.6	0.82
Ethylbenzene	10.4	10.6	10.1	5.4	0.00
p,m-Xylene	7.46	7.50	6.28	2.00	0
Styrene	25.86	24.47	22.97	−7.17	0
Benzene	13.5	11.5	8.3	−3.3	0.09

*:all precision estimates were calculated for VOCs species with concentrations exceeding three times the MDL.

We analyzed the selected VOCs at four monitoring sites, with simultaneous measurements using both PAS and on-line PAMS methods, as detailed in Table 3. At the Jongno and Guro sites, the VOCs concentrations obtained from passive and active sampling were in close agreement for most compounds, with an average difference of less than 20 % for all except AROx, which showed a discrepancy of up to 60 %. In

Table 3
Comparison of mean concentrations (in ppbv) between PAS and online-PAMS measurements at four stations and p-value analysis for similarity test. p-values higher than 0.05 indicate no significant difference between the measurement methods at a 95% confidence level.

Species	Method	Jongno	Guro	Gangseo	Gwangjin	p-value
Toluene	PAS	2.45	2.36	3.03	1.72	0.82
	Online-PAMS	2.91	2.68	2.85	0.81	
Benzene	PAS	0.28	0.30	0.30	0.24	0.28
	Online-PAMS	0.37	0.23	0.14	0.03	
Isoprene	PAS	0.07	0.16	0.19	0.09	0.08
	Online-PAMS	0.06	0.04	0.08	0.05	
Alkanes	PAS	7.85	7.75	19.79	5.18	0.26
	Online-PAMS	8.99	6.16	10.03	2.64	
Olefines	PAS	0.98	0.86	0.88	0.73	0.01
	Online-PAMS	0.71	0.65	0.62	0.63	
AROx	PAS	2.23	2.17	2.42	1.67	0.08
	Online-PAMS	0.97	1.80	2.09	0.63	

*AROx; aromatic compounds excluding toluene and benzene.

contrast, at the Gangseo site the measurements differed significantly, with discrepancies averaging 50 %, probably due to localized emission sources in the vicinity.

To assess the degree of agreement between passive and active sampling methods, we conducted statistical analyses on the concentrations of VOCs common to both methods, utilizing the p-value. The analysis showed that, for the most compounds, the p-value exceeded 0.05, indicating no significant difference in measurements between the two methods. However, the olefines stood out, showing a consistent overestimation by 24 % in the passive sampling data across all sites when compared to active sampling.

3.2. *Temporal variation*

Fig. 2 depicts the levels of total volatile organic compounds (TVOCs) measured in ppbv at five PAMS and 25 PAS observations throughout the year. Urban PAMS measurements at Jongno, Gangseo, and Guro sites exhibited significant seasonal variations, whereas Gwangjin district and background site of Bukhan mountain showed no seasonal changes. Active PAMS measurements generally peaked in late fall and remained relatively stable in other seasons. In Gangseo district, TVOCs concentrations reached nearly 30 ppbv in October. However, PAS did not reveal clear seasonal trends, as no measurements were taken in October and November. PAS recorded higher concentrations during the summer months compared to September and February, with overall higher levels in summer than active measurements. Despite this, the PAS consistently fell within the range of the four urban PAMS measurements, effectively capturing both seasonal variations and spatial differences in TVOCs levels at the different sites. This agreement was further supported by the intercomparison results discussed earlier in Table 3, which indicates that PAS and active measurements yielded statistically similar results.

Among the VOCs species representing specific emission sources, isoprene, mainly emitted from vegetation, had concentrations near the detection limit (0.14 ppbv) during the winter months, but increased significantly to about 1.06 ppbv at the mountain site during the summer months. Toluene and xylenes, emitted from traffics and solvent use in Korea, showed 18–72 % higher concentrations in summer compared to winter. In contrast, ethane concentrations increased by 213 % in winter, correlating with increased heating demand. Benzene concentrations also increased significantly in winter (171 %), likely due to long-range atmospheric transport and increased fossil fuel emissions (Simpson et al., 2020).

3.3. *Spatial distribution*

The spatial distribution of VOCs in the Seoul area was obtained through PAS observation, and the results are shown in Fig. 3. It shows the seasonal spatiotemporal distribution of TVOCs concentrations in Seoul from September 2022 to June 2023, observed at three different periods: February, June, and September. Consistently elevated concentrations are observed in the southwestern region during all three observation periods. This high VOCs area was likely due to the emission of VOCs from heavy traffic, automobile paint shops, and laundry facilities, which are densely clustered in this area (Statistics Korea, 2022). In particular, the westernmost sector of Seoul, which was characterized by the highest levels of VOCs, was likely due to the cumulative effects of local VOCs-emitting businesses and the transport of pollutants from upwind regions of Seoul, including the Korea's largest metropolitan landfill and the airport (Kim et al., 2021b; Lim et al., 2018).

Although the overall spatial distribution of VOCs remained fairly constant throughout the seasons, distinct variations in specific areas were evident at different times. For instance, high VOCs concentrations were often recorded in central Seoul during June. This increase can be linked to the numerous small-scale commercial facilities using organic solvents in the area, which tend to evaporate more during the warmer summer months. Consequently, these conditions likely lead to more pronounced regional disparities in VOCs concentrations when compared to the levels observed in February and September (Baudic et al., 2016; Xu et al., 2023).

Isoprene, a major indicator of BVOCs among VOCs (Guenther, 2013), showed high concentrations in forested areas, especially on the outskirts, reflecting Seoul's basin-shaped topography, surrounded by the Bukhan, Dobong, Inwang, and Gwanak mountains (Fig. 4-a). Conversely, the central urban areas with less forest cover had relatively low concentrations, but BVOCs near Acha mountain in the eastern center of Seoul are higher than other urban areas. Among anthropogenic VOCs, toluene, an indicator of vehicle emissions and solvent use, exhibited a wide concentration distribution across Seoul, particularly in

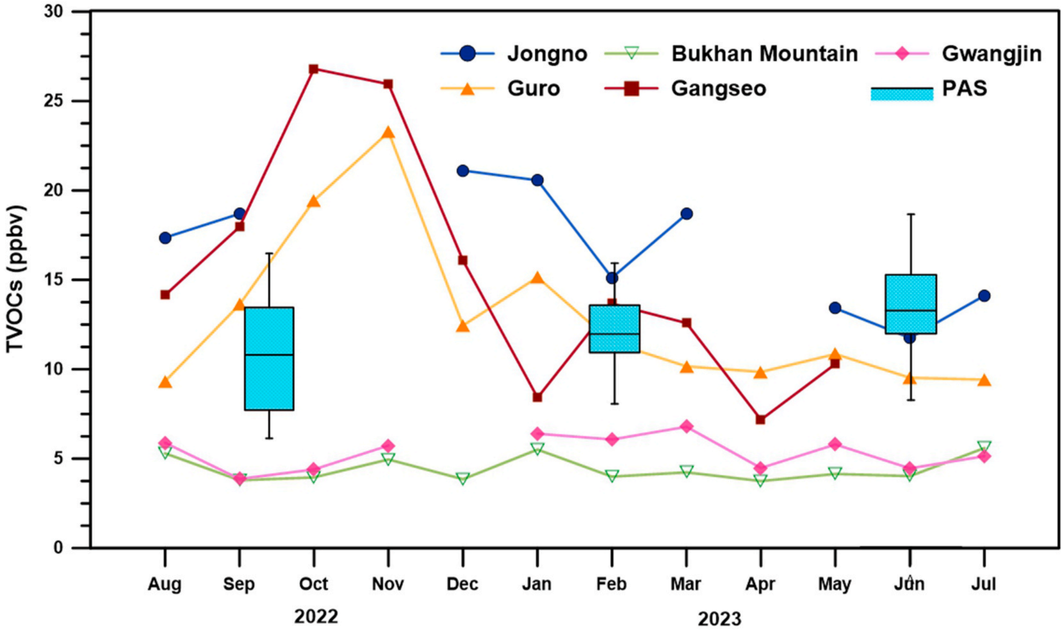

Fig. 2. Monthly variation of total VOCs concentrations measured by PAS and at five PAMS stations including a background site (Bukhan mountain) marked by green line with inverted triangle over a year (2022–2023).

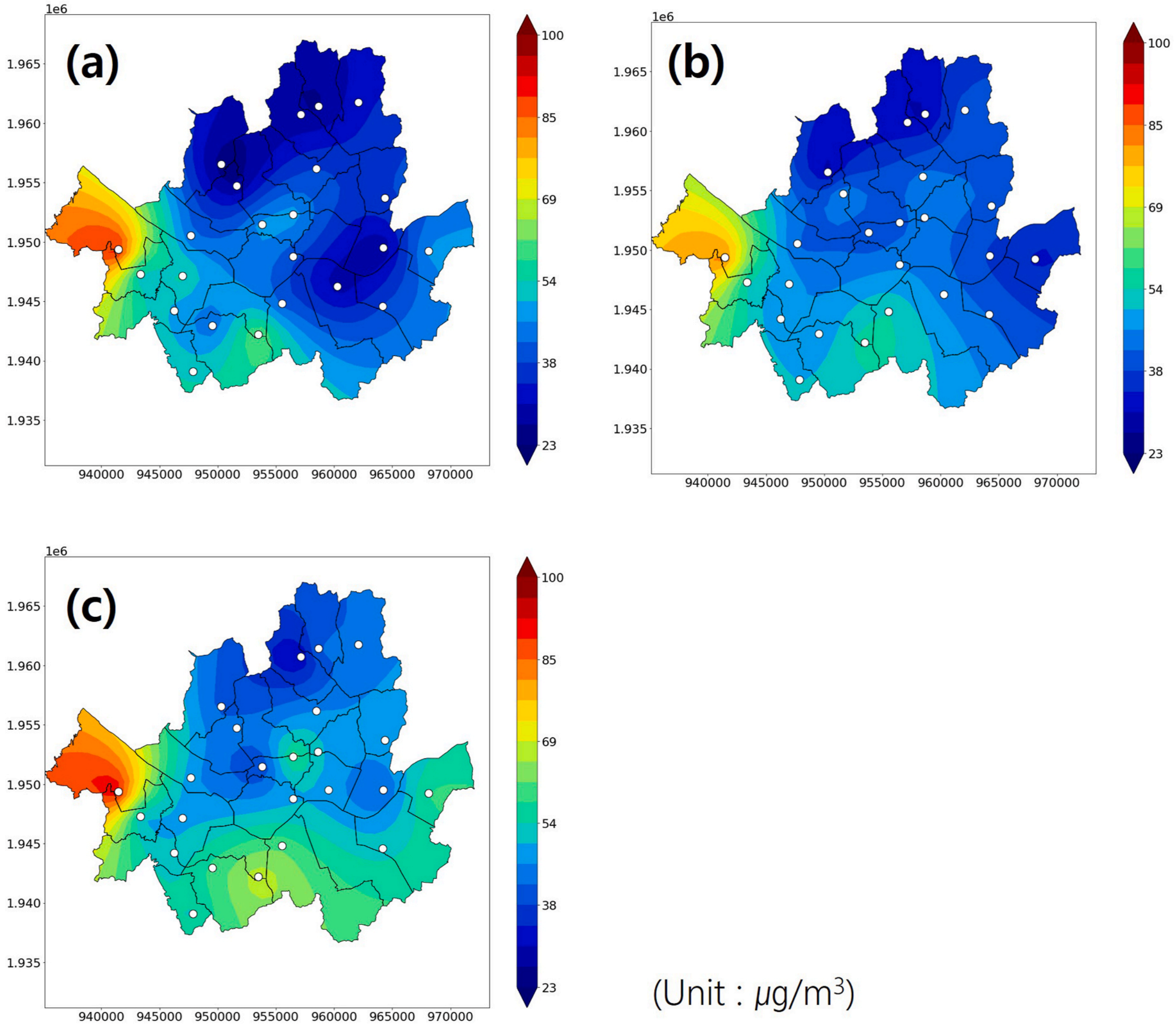

Fig. 3. Spatial distribution of TVOCs concentrations (μg/m^3) measured by PAS during the observation period using UTM coordinate of Seoul: (a) September 2022; (b) February 2023; (c) June 2023. White circles on the map represent the PAS measurement locations.

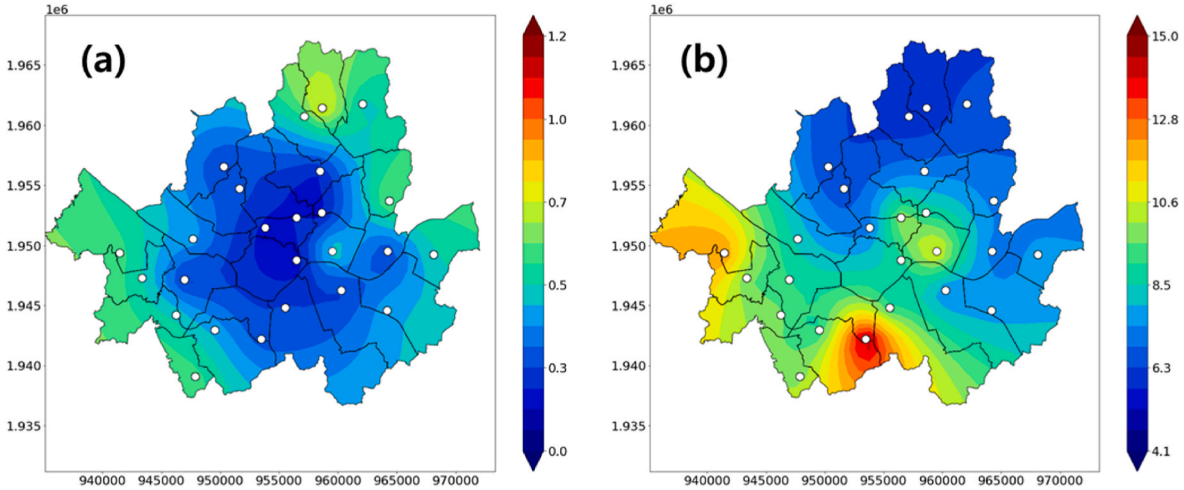

Fig. 4. Spatial distribution of mean concentrations (μg/m^3) of Isoprene (a) and Toluene (b) measured by PAS over the entire observation periods using UTM coordinate of Seoul.

the central and southwestern regions (Fig. 4-b), reflecting its widespread sources. The dual-source nature of toluene is evident in the spatial distribution of TVOCs derived from our PMF analysis of both area sources (Fig. 6) and road use impacts (Fig. 7). These hotspot areas are known to be major transportation routes and areas with high densities of printing and auto repair shops that use solvents extensively. In the next section, the PMF analysis allows us to more comprehensively describe the spatial distribution of solvent use and vehicle emissions in Seoul. This integrated approach allows us to compare the spatial distributions of TVOCs source strengths, such as fugitive solvent use and vehicle emissions, with current emission inventories (CAPSS).

3.4. PMF analysis

Using the VOCs species measured by PAS, a PMF analysis was performed, resulting in five distinct emission sources. The first emission source delineated from the PMF analysis manifested a significant contribution from major substances typically emitted by gasoline vehicles, including propylene, 1-butene, 2,2,4-trimethylpentane, styrene, toluene, and 1,3,5-trimethylbenzene (Ho et al., 2009; Schauer et al., 2002; Watson et al., 2001) (Fig. 5). In this study, propylene was identified as the most prominent indicator of motor vehicle emissions, whereas benzene exhibited minimal influence from traffic sources. This finding highlights the distinct emission signatures in Seoul compared to other areas. This suggested that mobile sources contribute 16.3 % of the measured VOCs in Seoul.

The second source was inferred to be from small scale urban laundry and printing, including decane, 1,2,4-trimethylbenzene, n-undecane, n-

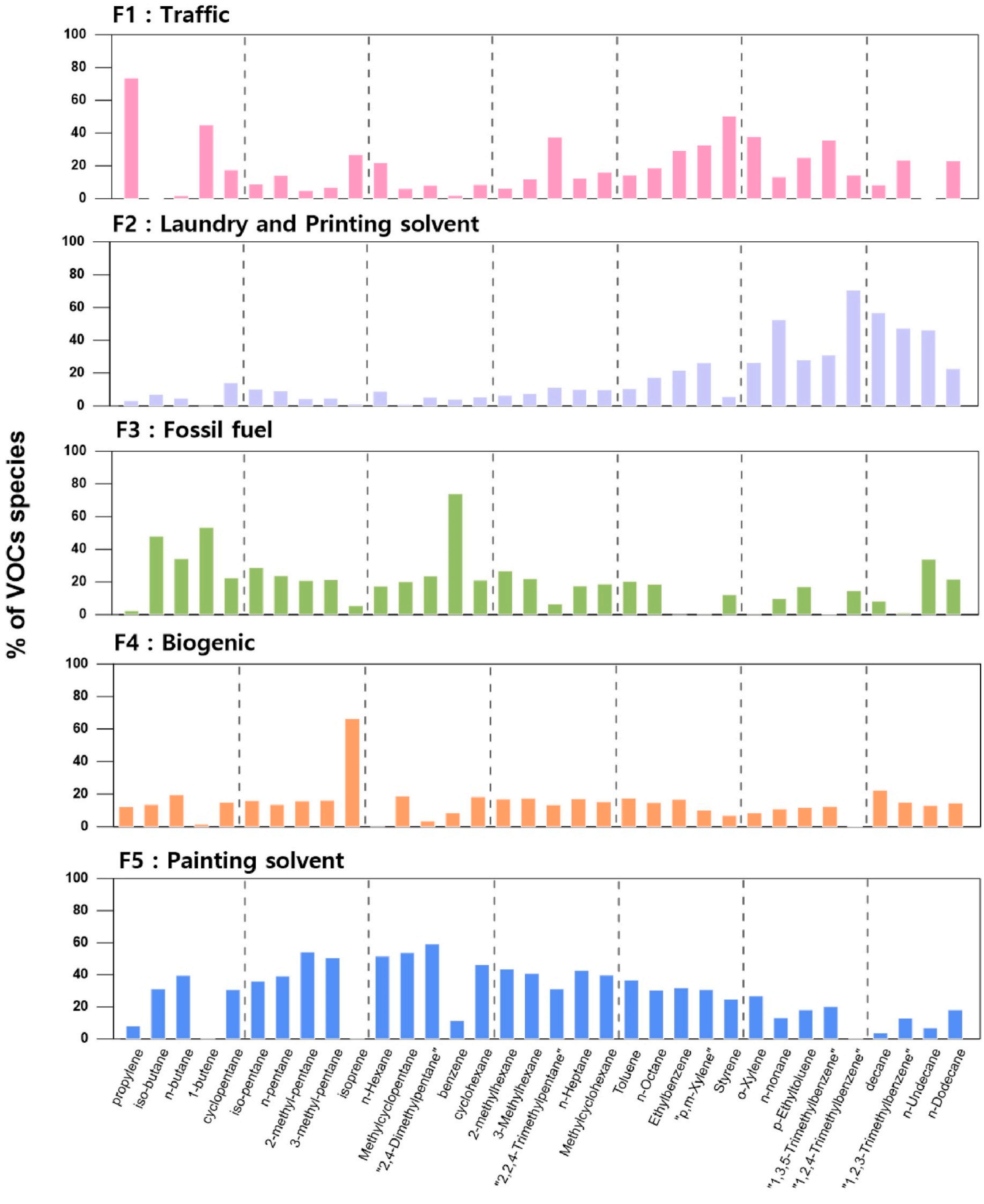

Fig. 5. Proportion of VOCs species attributed to various emission sources based on PMF analysis: Factor 1 (F1) -Traffic emission, F2-Laundry and Printing solvent, F3-Fossil fuel, F4-Biogenic and F5-Painting solvent.

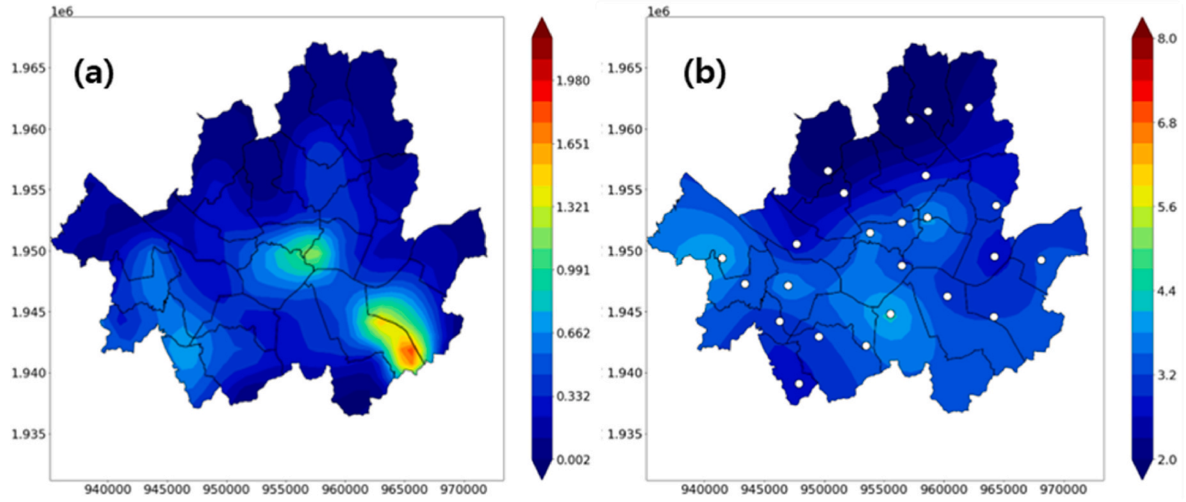

Fig. 6. Spatial distribution of area sources: (a) emission strength (moles $\sec^{-1}\mathrm{km}^{-2}$) derived from the CAPSS; (b) unitless normalized contribution acquired through PMF model factors following the PAS observation.

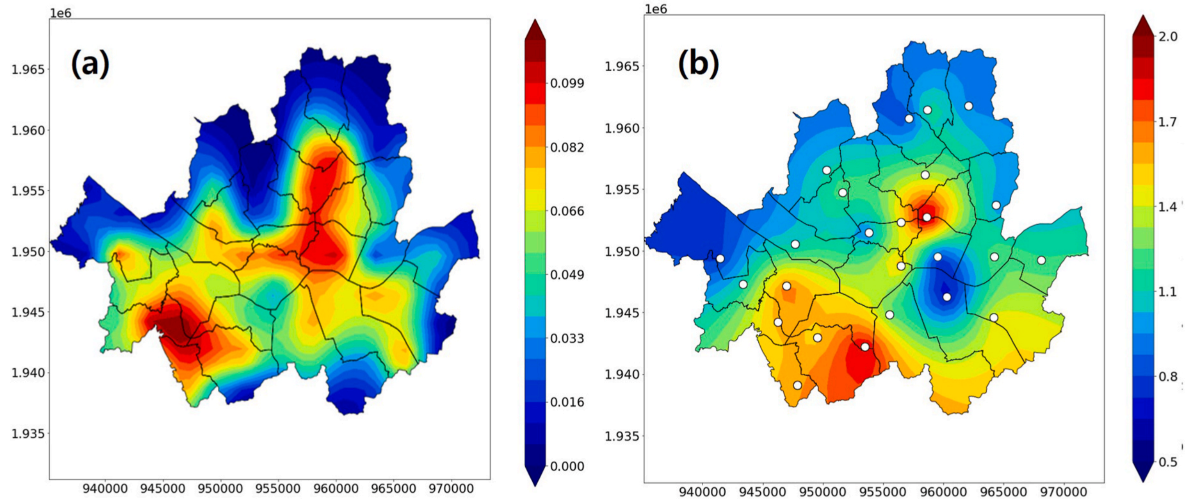

Fig. 7. Spatial distribution of road sources: (a) emission strength (moles $\sec^{-1}\mathrm{km}^{-2}$) derived from the CAPSS; (b) unitless normalized contribution acquired through PMF model factors following the PAS observation.

nonane, and xylene, contributing 14 % of the VOCs in Seoul. Printing processes emit a variety of high molecular VOCs during the drying and resin melting phases (Ahn et al., 2018; Betha et al., 2011; Steinemann et al., 2013).

The third source was identified as fossil fuel combustion, particularly from the use of heating fuels, primarily characterized by benzene, isobutane, n-butane, and 1-butene. Benzene also serves as an indicator of long-range transport. The seasonal distribution shows elevated concentrations during the winter months, corresponding to increased heating fuel use, contrasted with lower levels in September and June (Dimitriou and Kassomenos, 2020; McDonald et al., 2018).

Isoprene, the fourth pollutant source, indicated natural emissions, mainly from biogenic VOCs emitted by vegetation, and show significant seasonal variations (Bai et al., 2017; Mozaffar et al., 2018; Yáñez-Serrano et al., 2015). Higher concentrations were observed outside of downtown Seoul, especially in summer, which was attributed to forested areas.

The fifth and largest VOCs source included toluene, 2,4-dimethylpentane, 2-methylpentane, xylene, and cyclohexane, which were attributed to solvent emissions from painting and account for 33 % of the VOCs concentration in Seoul. Toluene and xylene, prominent components, were widely used in painting processes in various commercial and domestic sectors. Spatial distribution shows elevated concentrations in areas such as Gangseo district, Jongno district, and Seongdong district, which corresponded to concentrations of printing and painting facilities. These facilities, which are an integral part of synthetic industrial processes, are used to coat the surfaces of automobiles, machinery, electronic components, and household electronic devices, using various organic solvents and pigments, including aromatic compounds and esters (Liu et al., 2008; Watson et al., 2001; Zheng et al., 2013).

3.5. CAPSS emission inventory

The CAPSS is a comprehensive database platform based on an air pollutant emission inventory in Korea. This system systematically aggregates and manages the emission inventories of nine major air pollutants (TSP, $PM_{2.5}$, PM_{10}, SOx, NOx, VOCs, NH_3, CO, BC) from point, area, and road sources to provide the essential tools for air quality policy formulation and implementation (Choi et al., 2022). In the previous section, we found five different emission sources using the PMF, of which painting, fossil fuel, and printing facility sources can be grouped together as area sources in the CAPSS emission classification. We compared the spatial distribution of these PMF derived area emission sources (Fig. 6-b) with those in CAPSS (Fig. 6-a). The spatial distribution of VOCs, as determined by the PAS derived PMF area sources, revealed concentration peaks in the south-central and Gangseo districts of Seoul, indicating relatively high emission densities in these areas, consistent with CAPSS data. However, unlike the CAPSS data, the PAS measurements did not identify a significant emission source in southeastern Seoul. This discrepancy is likely due to the presence of several large-scale automotive paint shops in that area, which were not detected in this study because they are located more than 5 km away from the closest PAS measurement site. This exclusion of certain VOCs hotspots could result in an underestimation of the ambient VOCs levels measured by PAS.

The spatial distribution of VOCs concentrations from road source emissions in the CAPSS spatial inventory (Fig. 7-a) was compared with the results of the PAS derived PMF model (Fig. 7-b). The spatial distribution of road traffic emissions derived from the PMF analysis was largely consistent with the CAPSS data, showing elevated concentrations in the central and southern parts of Seoul, which are areas with heavy vehicle traffic. However, there are significant discrepancies in some areas, such as the eastern part of Seoul. One factor contributing to this discrepancy is that the PAS monitoring sites in eastern Seoul were relatively far from major roads, minimizing the influence of road traffic emissions in these areas. Additionally, there is the challenge of clearly separating the signals from traffic sources and area sources, as discussed earlier with toluene. It is likely that the first source identified in our analysis, attributed to vehicle exhaust, also had characteristics of common combustion sources, adding complexity and uncertainty to our results. Consequently, a direct comparison of our PMF results with the

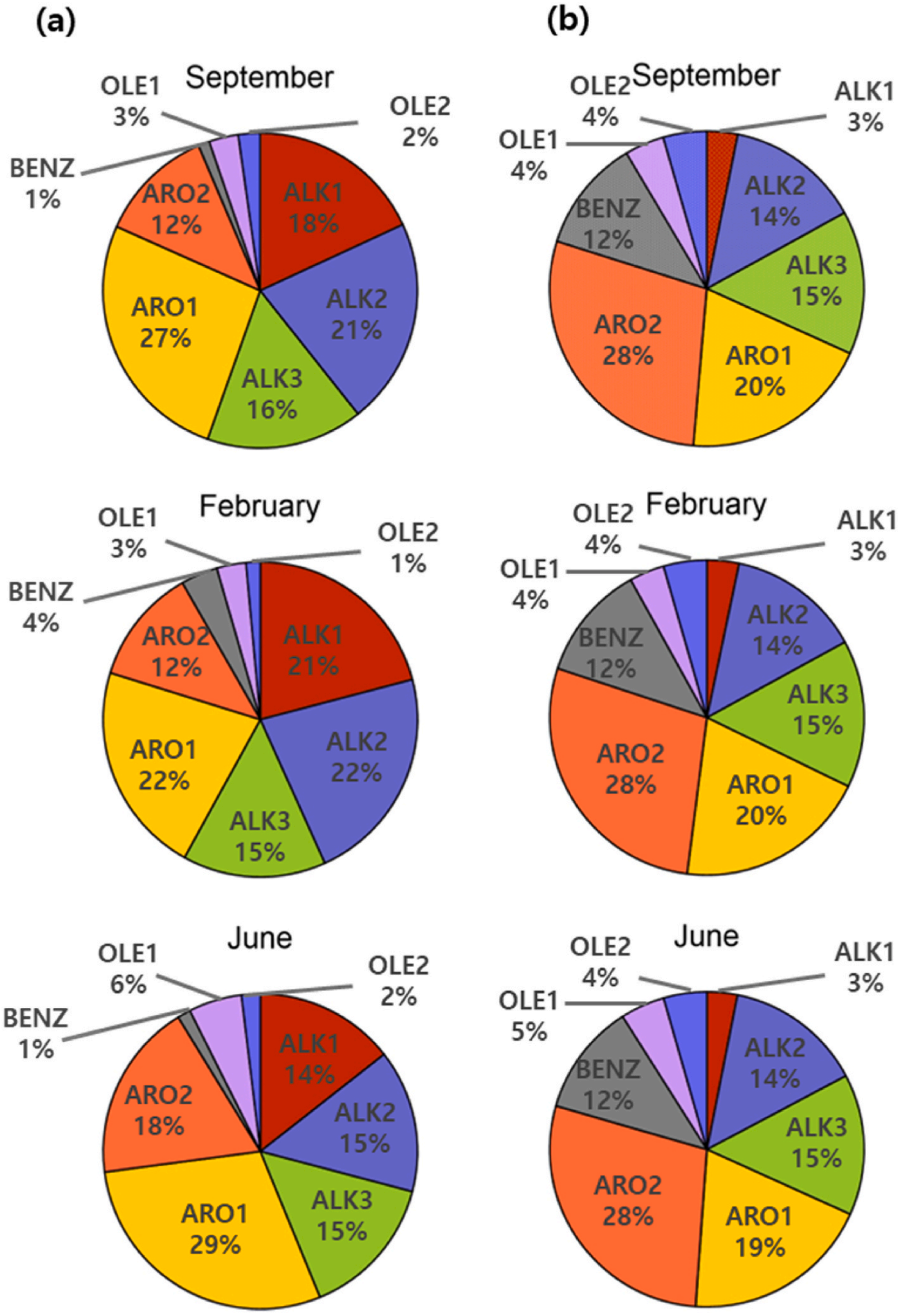

Fig. 8. Comparison of VOCs composition over each observation period: (a) as obtained from PAS measurements; (b) as modeled by CAPSS.

CAPSS data may not be entirely appropriate, and discussions drawn from this comparison should be interpreted with caution.

3.6. VOCs compositions

VOCs are a diverse group of organic chemicals that are often classified into three main types based on their chemical reactivity and structure: alkanes, aromatics, and olefins (Yuan et al., 2012). Each type has similar atmospheric lifetimes and reactivities. In our study, we have further refined this categorization into eight specific groups of VOCs: three types of alkanes (ALK1, ALK2, ALK3), two types of aromatics (ARO1, ARO2), benzene (BENZ), and two types of olefins (OLE1, OLE2). This detailed classification improves the accuracy of our comparison between the observed VOCs species and those recorded in the CAPSS emission inventory. A full description of the VOCs species within each group is provided in Supplement S4.

Fig. 8 compares the VOCs composition detected by PAS with that reported in the CAPSS database over the same period. According to the PAS data, alkanes represent 52 % of emissions (18 % for ALK1, 19 % for ALK2, 15 % for ALK3), aromatics 40 % (26 % for ARO1, 14 % for ARO2), benzene only 2 %, and olefins 6 % (4 % for OLE1, 2 % for OLE2). However, CAPSS shows a different distribution: alkanes make up 32 % of the VOCs emissions (3 % for ALK1, 14 % for ALK2, 15 % for ALK3), aromatics 48 % (20 % for ARO1, 28 % for ARO2), benzene 12 %, and olefins 8 % (4 % for OLE1, 4 % for OLE2).

Especially, there is a notable discrepancy in benzene levels between observations and emission inventory. The CAPSS inventory displayed a consistent benzene contribution of 12 % across all seasons, suggesting an inability of CAPSS to accurately capture the dynamic changes in atmospheric benzene concentrations. In most urban areas, the major source for benzene is the gasoline exhaust (Hong-li et al., 2017).The average ratio of toluene to benzene emissions (T/B ratio = 2.2) was found in vehicle exhaust in Korea (Mun et al., 2018). As traffic usually remains the main source of VOCs in urban areas, ratios of toluene and benzene have been used before to estimate the age of urban air mass influenced by vehicular exhaust. According to the CAPSS VOCs emission inventory, benzene accounts for a significant proportion (14 %) of the VOCs composition, highlighting vehicle emissions as the dominant source of VOCs, as shown in Fig. 8-b. However, the observed benzene compositions in Seoul are relatively low, with an average T/B ratio of 8.5, which is significantly higher than that attributed to vehicle emissions. This elevated T/B ratio in Seoul has been consistently observed in other studies, including aircraft measurements during the KORUS-AQ campaign (Simpson et al., 2020), which reported an average T/B ratio of 7.6. These results suggest both a potential overestimation of benzene emissions from traffic sources and a significant emission influence of other aromatic sources, presumably solvent and industrial use in Seoul, a factor not adequately considered in the current CAPSS inventory. This oversight also implies a potential underestimation of VOCs emissions in Seoul.

PAS measurements revealed a pronounced seasonal fluctuation in benzene concentrations, peaking at 4 % during winter and diminishing to 1 % in both summer and fall. This pattern was well matched with the documented seasonal variability of benzene concentrations in Seoul, as reported in previous studies (Anthwal et al., 2010; Lee et al., 2023). Also, in the CAPSS data, aromatics (ARO1 and ARO2) accounted for almost half of all VOCs throughout the year. Specifically, xylene (ARO2) was reported to be between 23 and 28 %, exceeding the toluene-dominated ARO1. However, PAS results show that ARO1 contributes 22–29 %, significantly more than ARO2's 12–18 %.

The composition of alkanes also varied considerably. For example, low molecular weight alkanes (ALK1) were observed at 14–21 % of total VOCs, significantly higher than the 3 % observed by CAPSS. High molecular weight alkanes (ALK3) were in close agreement between the two datasets at about 15 %. However, for ALK2, the observed and CAPSS values differed significantly, especially in fall and winter, with a seasonal variation of more than 50 %. Seasonal changes in olefin composition did not show significant differences between observations and CAPSS, in contrast to the other VOCs species.

3.7. Observational assessment of VOCs emission inventory

In this research, we modeled the concentrations of VOCs using both the Box model (Eq-7) and the Gaussian plume model (Eq-8) to quantitatively evaluate emissions rates against actual measurement (Hanna et al., 1982). To calculate ambient VOCs concentration (C) with the Box model (Eq-7), we needed several inputs: the rate of VOCs emissions (Q_a), the wind speed (u), Seoul's longitudinal length scale (Δx), the height of the Planetary Boundary Layer (PBL, z_i), and background concentration (C_b). On the other hand, the Gaussian plume model depended on a different set of parameters, notably the vertical dispersion parameter (σ_z), which varies with the class of atmospheric stability.

$$(C - C_b) = \frac{\Delta x \bullet Q_a}{u \bullet z_i} \tag{Eq-7}$$

$$(C - C_b) = \left(\frac{2}{\pi}\right)^{1/2} \frac{\Delta x \bullet Q_a}{u \bullet \sigma_z} \tag{Eq-8}$$

These models helped assess the ambient VOCs concentrations once the required inputs, such as VOCs emission rate, meteorological parameter including wind speeds for Seoul and background VOCs concentrations, are known. We calculated the spatially average emission rates for VOCs species using the most recently updated 2021 CAPSS emission inventories (Kim et al., 2024) over the Seoul and background VOCs concentrations were obtained from the monthly averages of VOCs observed in Bukhan Mountain background site, as presented in Supplement S5. We collected relevant meteorological information, such as the height of the PBL and atmospheric stability, as monthly averages from the Osan Meteorological Station, covering a decade from 1983 to 1992 (Choi and Baek, 1998).

Fig. 9 shows the TVOCs median concentration ranging from 11 to 13 ppbv obtained from PAS measurements over three different time periods, presented using box plots. It also shows the estimated monthly ambient TVOCs concentrations derived from both the Box model (indicated by a red line) and the Gaussian model (indicated by a green line) based on CAPSS emissions and weather data. Both models gave similar results, averaging between 12 and 15 ppbv. However, the Box model showed a more pronounced seasonal variation, with higher concentrations in summer and winter and lower levels in spring and autumn. This greater variability in the box model was primarily due to notable seasonal changes in the height of the PBL, surpassing the seasonal variations of vertical dispersion parameter (σ_z).

Comparisons between observed and modeled concentrations estimates generally show good agreement, particularly for summer and winter, where observed concentrations fell within the ranges predicted by both models, indicating strong consistency. However, our model only accounts for dilution effects and does not include photochemical degradation of VOCs, which could lead to overestimation of modeled VOCs levels, particularly in summer when photochemical activity is significantly higher than in winter. Our models include background concentrations to account for transport effects from external sources, especially from upwind sources west of Seoul, considering their influence on spatial PAS measurements. But as mentioned above, the PAS data failed to identify high emission zones in the southeast of Seoul, which are evident in the CAPSS spatial inventories (Fig. 6). This omission of specific VOCs hotspots could lead to the underestimation of ambient VOCs levels measured by PAS.

In summary, there is good agreement between PAS observations and modeled values. However, the potential for overestimation by the models and underestimation by the PAS observations suggests that actual ambient VOCs concentrations could exceed those predicted by our models based on the CAPSS emission inventory, especially during

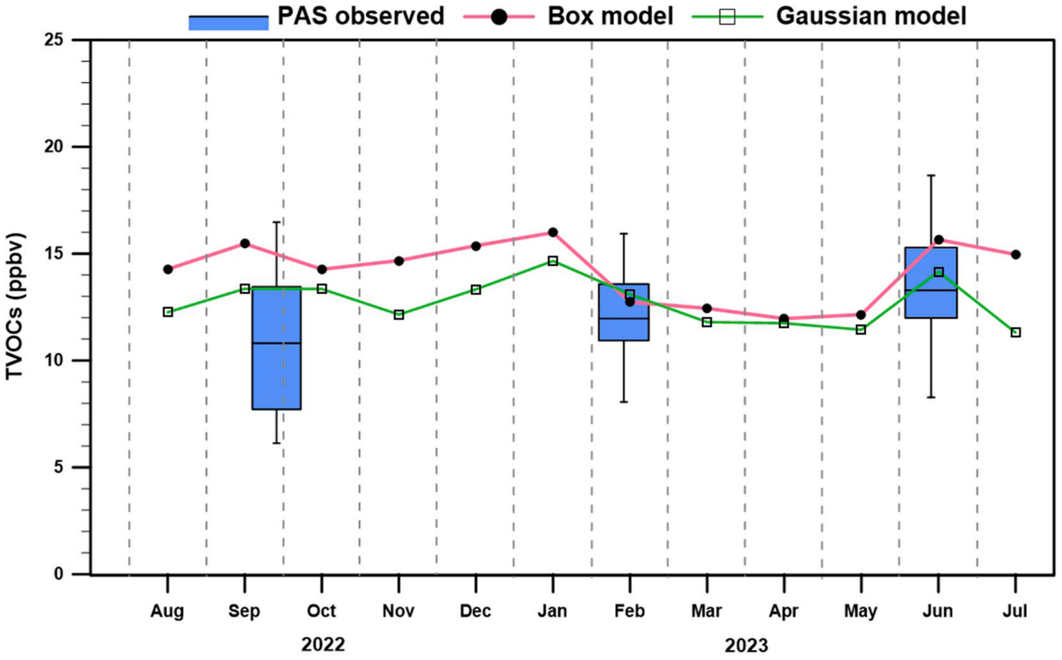

Fig. 9. Time series comparison of TVOCs concentrations: observed PAS measurements (boxplot) versus box model simulations (red line with solid circles) and gaussian model predictions (green line with open squares).

the summer months. Although we faced limitations in quantifying the shortcomings of the CAPSS emission inventory in accurately simulating actual VOCs levels in Seoul, we have indirectly shown that the CAPSS data might not fully capture all VOCs sources in the city. To improve the accuracy of VOCs emission inventory in Seoul, future research should incorporate more comprehensive spatial observations of VOCs and include photochemical reactions in the models. Nevertheless, the use of PAS to map the spatial distribution of VOCs confirmed its effectiveness as a tool to improve the assessment of CAPSS emission data within the study area.

4. Conclusion

This study conducted a comprehensive assessment of VOCs in Seoul using both PAS and active sampling at five PAMS monitoring stations. The quantitative and compositional consistency of the PAS method with online PAMS was statistically validated, effectively capturing the spatio-temporal behaviors of VOCs in Seoul.

Spatial analysis of VOCs by PAS revealed significant influences from localized and transported sources in the southwestern region of Seoul, as well as vehicular emissions in the urban center. Comparisons between PAS-measured spatial distributions and those derived from CAPSS emission data showed close agreement, confirming the effectiveness of PAS for long-term spatial assessment of VOCs. This comparison provided a strong basis for refining the CAPSS spatial emission inventories.

Using the PMF model with PAS observations, the study categorized VOCs emission sources into five types: printing and laundry, road traffic, fossil fuel, painting, and biogenic. This categorization allowed a detailed comparison with CAPSS data, which generally agreed, but also highlighted significant discrepancies in spatial distribution, especially in southeastern Seoul. These results underscored the need for more refined denser PAS observations in these areas.

The study revealed important discrepancies in VOCs speciation between modeled data and observations. PAS observations showed a higher proportion of alkanes and more pronounced seasonal variations in benzene concentrations compared to CAPSS data. Specifically, PAS data indicated that alkanes accounted for 49 % of the VOCs, while non-benzene aromatics and benzene accounted for 40 % and 2 %, respectively. In contrast, CAPSS estimated alkanes at 32 %, non-benzene aromatics at 48 %, and benzene at 12 %. This suggested that CAPSS may overestimate the presence of aromatics and may not capture seasonal variations, particularly for benzene, in its inventories. TVOCs concentrations measured by PAS, which ranged from 11 to 13 ppbv, were slightly lower than the model predictions of 12–15 ppbv derived from CAPSS data. However, the exclusion of emission hotspots in the PAS measurements and the omission of photochemical losses in the models suggested that actual ambient VOCs levels could be higher. Additionally, if models included the photochemical loss of VOCs, the predicted concentrations would likely be significantly lower than our present estimates, especially in summer. These two factors could further increase the underestimation of VOCs emissions in the current CAPSS inventory.

We successfully incorporated the first long-term spatial observations of PAMS VOCs using PAS to validate the VOCs emission inventory in Seoul. This approach has demonstrated the value of PAS in mapping the spatial distribution of VOCs and assessing the accuracy of CAPSS emission data. However, to further improve the accuracy of VOCs spatial emission assessments, future research should aim to expand the scope of spatial VOCs observations and integrate photochemical reactions into the models. By doing so, we can achieve a more comprehensive understanding of VOCs emissions and their behavior. The findings underscore the potential for significant advancements in VOCs monitoring and management, ultimately contributing to better air quality and public health outcomes in Seoul.

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CRediT authorship contribution statement

Jimin Lee: Writing – review & editing, Writing – original draft, Visualization, Investigation. **Meehye Lee:** Writing – review & editing, Investigation, Data curation. **Limseok Chang:** Supervision, Funding acquisition. **Sun-A Shin:** Resources, Project administration. **Kwangrae Kim:** Validation, Formal analysis, Data curation. **Yongsuk Choi:** Validation, Formal analysis, Data curation. **Hakmyeong Lim:** Validation, Formal analysis, Data curation. **Sung-Deuk Choi:** Methodology, Formal analysis. **Gangwoong Lee:** Writing – review & editing, Writing – original draft, Software, Methodology, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

5. Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.atmosenv.2024.120857.

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