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Identification of Volatile Organic Compounds from Gradual Emission Sources in Indoor Workplace Air Using Sequential Sampling and Multivariate Analysis

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Volatile organic compounds (VOCs) in indoor air are emitted from a wide variety of consumer products and building materials and are routinely inhaled through daily activities. Owing to their effects on human health, identifying VOCs from emission sources associated with indoor air pollution is important for effective exposure management. In particular, VOCs from time-varying emission sources, such as daily activities including cleaning, cooking, and eating, often exhibit complex patterns and require sophisticated methodologies for accurate source identification. This study applied sequential air sampling combined with multivariate analysis to identify VOCs from gradual emission sources, one of the time-varying types, in a workplace. Non-targeted analytical data from sequential indoor air samples were analyzed using principal component analysis (PCA) to visualize indoor air quality patterns. The samples were grouped into three clusters: Group I was characterized by decamethylcyclopentasiloxane (D5), possibly associated with the application of personal care products during the hours when people were present in or near the room; Group II was characterized by toluene, ethyl acetate, and trichloroethylene; Group III was located near the center of the PCA score plot. Notably, individual VOCs found by our method were major components of the temporal changes in total VOC observed during multi-day sampling. This approach can be useful for identifying VOCs from gradual emission sources, particularly those related to occupant activities and product use.

Key words indoor air quality, volatile organic compounds, gradual emission sources, sequential sampling, multivariate analysis

INTRODUCTION

Humans inhale approximately 10–15 m^3 of air per day, about 90% of which originates from indoor environments.[1)] Volatile organic compounds (VOCs) in indoor air originate from a wide variety of consumer goods and building materials and are routinely inhaled in daily life.[2–3)] In particular, VOCs eluting between *n*-hexane and *n*-hexadecane on a non-polar column in gas chromatography, total volatile organic compounds (TVOC), are a key target in indoor air assessment.[4)] Although VOC concentrations in indoor air are generally low, long-term exposure has been associated with adverse health effects, including respiratory symptoms and irritation.[5–8)] Accordingly, identifying VOCs from emission sources associated with indoor air pollution is important for exposure management.

Emission sources in indoor air can be broadly categorized into two types, based on their emission characteristics. Some sources emit continuously and stably, such as furniture and building materials,[9–10)] whereas others produce short-term concentration changes associated with daily activities such as cleaning, cooking, and the application of cosmetics and household products.[11)] In this study, the former are referred to as steady emissions and the latter as time-varying emissions. Time-varying emissions have been further described as including changes associated with transient activities or events, such as peeling citrus fruit, while others gradually change over several hours, such as personal care products, brought-in materials, and changes in ventilation.[12)] Thus, indoor VOC emissions can be re-characterized as steady emissions and time-varying emissions, with the latter comprising transient emissions and gradual emissions.

The emission behavior of source types can be influenced by environmental factors, such as temperature and humidity,[13)] time of day,[14)] ventilation conditions,[15)] and photocatalytic oxidation.[16)] The first step in elucidating the characteristics of the emission sources is to accurately identify the VOCs originating from each source. However, such identification requires sophisticated analytical techniques. In particular, identifying VOCs derived from time-varying emission sources is challenging because these emissions often appear as temporary concentration increases.

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Multivariate statistical approaches have been applied to examine patterns of VOC occurrence and their relationships with potential indoor sources. Guo evaluated VOC concentrations in Hong Kong homes and statistically apportioned the observed VOCs among several potential source categories.[17] Rösch *et al*. applied principal component analysis (PCA) to VOC data collected from residential environments to identify groups of compounds with similar concentration patterns and examined their relationships with potential sources and residential characteristics.[18] These studies demonstrated the utility of multivariate analysis for interpreting complex indoor VOC profiles. However, time-varying changes in VOC profiles remains insufficiently characterized using multivariate analysis.

In the present study, we focused on gradual emissions, one of the time-varying types, that could influence on time-averaged concentrations, and indoor air samples were sequentially collected from a workplace using a sequential tube sampler. The samples were analyzed by thermal desorption-gas chromatography–mass spectrometry (TD–GC–MS) to visualize indoor VOC profiles, and the resulting non-targeted data were subjected to PCA to systematically identify the key VOCs derived from gradual emission sources (Fig. 1).

MATERIALS AND METHODS

Chemicals Standard solutions were prepared using a 48 Component Indoor Air Standard solution (1000 μg/mL; SUPELCO, Bellefonte, PA, USA) for ethyl acetate, benzene, trichloroethylene, and toluene, and a Cyclic Siloxanes Standard Solution (1 mg/mL each in acetone; Cat. No. 07019-96, Kanto Chemical Co., Inc., Tokyo, Japan) for decamethylcyclopentasiloxane (D5).

Sampling Site and Survey Period The study was conducted in a mechanically ventilated workplace at the National Institute of Health Sciences (NIHS) in Japan. The room was occupied by up to 10 people, with occupancy levels varying during working hours (approximately 9:00–17:00 h), and the air exchange rate was maintained at least 2 h^{-1}. The room had a floor area of 114.3 m^2. The flooring consisted of carpet installed over a concrete substrate. The walls (total surface area: 106.9 m^2) were constructed of gypsum board with vinyl wall covering on light-gauge steel framing and concrete backing. The ceiling, with an area of 114.3 m^2 and a height of 2.7 m, was finished with decorative rock wool acoustic panels mounted on a light-gauge steel framework. The room was equipped with six ventilation outlets and four air-conditioning units. The air samples were collected at a height of 1.0 m above the floor and at distances of 1.0 m and 2.5 m from the wall (Fig. S1).

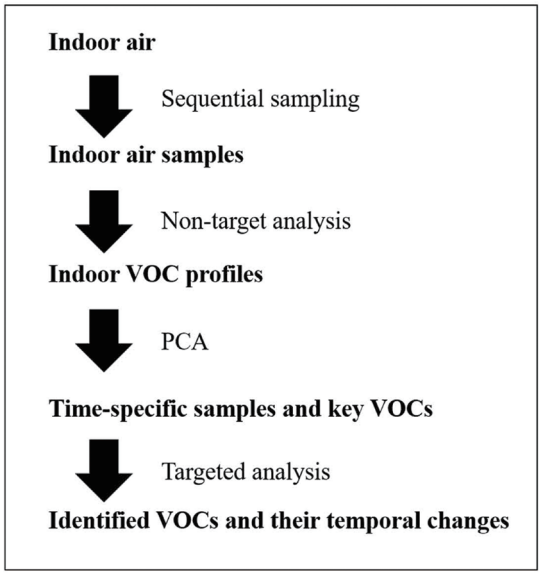

Fig. 1. Workflow of the Research.

Sampling Procedure The sampling condition was conducted in accordance with the "Manual for Measuring Indoor Air Chemical Substances" set by the Ministry of Health, Labour and Welfare (MHLW),[19] with a higher flow rate (10 mL/min) and a shorter sampling duration (5 h), which were sufficient to capture diverse VOCs without breakthrough.[20] Briefly, the VOCs were collected using Tenax TA SafeLok™ stainless steel tubes (Markes International Ltd., England, UK). Prior to sampling the air, the tubes were conditioned using TC-20 (Markes International Ltd., England, UK), heated at 100°C for 1 h, then at 300°C for 2 h, aerating with nitrogen at approximately 50 mL/min. Air sampling was performed at 10 mL/min for 5 h using a PMP-001 pump (Sibata Scientific Technology Ltd, Tokyo, Japan) performed sequentially for two 5-day periods, using an STS25/STS-25 sequential tube sampler (PerkinElmer Inc., MA, USA), allowing two independent weekday–weekend cycles to be captured. The time segments were: (1) from DAY1_9-14 (09:00–14:00, 28 March, Thursday) to DAY6_4-9 (04:00–09:00, 2 April, Tuesday), 2024; and (2) from DAY7_9-14 (09:00–14:00, 11 April, Thursday) to DAY12_4-9 (04:00–09:00, 16 April, Tuesday), 2024. Although Day 2 (March 29, 2024) was a weekday, no occupants were present near the sampling point.

TD–GC–MS Analysis The VOCs analysis was carried out using a thermal desorption unit (TD–30R) connected to a gas chromatograph-mass spectrometer (GCMS–QP2020NX), both from Shimadzu Corporation (Kyoto, Japan). The TVOC concentration was calculated as a toluene equivalent value based on internal standard methods using toluene-d_8, with the sum of the peak areas of the total ion current (TIC) chromatogram of the scan mode eluting at the retention time (RT) between *n*-hexane (RT 5.4 min) and *n*-hexadecane (RT 35.3 min).[4] The measurement conditions were as follows.

[TD]
Desorption: 300°C, 8 min, 50 mL/min
Cold Trap: −20°C
Trap Desorption: 280°C, 5 min
Line and Valve Temperature: 250°C

[GC]
Column: Rtx®-1 (0.32 mm i.d. × 60 m, 1 μm)
Carrier Gas: He, 40 cm/s
Split Ratio: 20:1
Oven Temperature: 40°C–(5°C/min) –280°C (4 min)

[MS]
Interface Temperature: 250°C
Ion Source Temperature: 200°C
Scan Range: *m/z* 35–450
Scan Rate: 10 Hz

Based on the PCA results obtained from the TIC scan data, selected VOCs contributing to the principal components were further analyzed by a targeted approach using selected ion monitoring (SIM). Ethyl acetate (RT 5.4 min, quantifier *m/z* 70; qualifier *m/z* 61), benzene (RT 6.7 min, quantifier *m/z* 78; qualifier *m/z* 77, 51), trichloroethylene (RT 7.6 min, quantifier *m/z* 95; qualifier *m/z* 97), toluene (RT 9.7 min, quantifier *m/z* 91; qualifier *m/z* 92, 65), and decamethylcyclopentasiloxane (RT 23.1 min, quantifier *m/z* 267; qualifier *m/z* 355, 73) were analyzed. The range of the calibration curve was 0.5–100 ng. The compounds were identified by comparison with authentic standards.

Data Processing and VOCs Quantification Deconvolution of TIC data on TD–GC–MS analysis was performed using AnalyzerPro® XD (SpectralWorks Ltd., Runcorn, UK). A total of 468 deconvoluted peaks were extracted under parameters as follows:

- Area threshold: 500
- Signal-to-noise ratio: 5
- Identification library: NIST
- Forward and reverse match thresholds: 650
- Confidence threshold: 65%

Multivariate Analysis The resulting data matrix consisted of 47 time-series samples (rows) and 468 chemicals (columns), where each variable represented the peak area of a deconvoluted compound. The data were imported into SIMCA® ver. 17 (Sartorius Stedim Data Analytics AB, Umeå, Sweden) for PCA, and then preprocessed using Pareto scaling.

Pearson Correlation Analysis The correlation coefficient (r) was calculated using the CORREL function in Microsoft Excel (Microsoft Corp., USA). The corresponding two-tailed *p*-value was calculated using the T.DIST.2T function based on the t-statistic ($t = r\sqrt{(n-2)/(1-r^2)}$) with $n-2$ degrees of freedom.

RESULTS AND DISCUSSION

Indoor air was collected from the workplace using a sequential tube sampler, with one sampling tube per 5 h interval, over two separate 5 day periods. The samples were analyzed using TD–GC–MS. Typical TIC chromatograms are shown in Fig. 2. TIC raw data were deconvoluted, and a time-series dataset of VOC peak areas was applied to the PCA.

In the score plot (Fig. 3), each point represents a 5 h integrated air sample, and proximity in the score space indicates similarity in the multivariate VOCs profile. The samples were grouped into three clusters: Group I [DAY1_9-14, DAY5_8-13; occupied weekday mornings], Group II [DAY2_20-1, DAY3_1-6, DAY3_6-11; from night to morning on a single day], and Group III [the others; situated near the origin in the PCA score space]. The first and second principal components (PC1, PC2) explained 26.2% and 19.5% of the total variance, respectively. Rösch *et al.* reported that PCA of 60 VOCs measured in 2,242 Germfan flats showed cumulative explained variance up to PC2 of 27.5%, with 18.75% for PC1 and 8.75% for PC2.[17] This report provides a useful reference for interpreting the range of explained variance ratio obtained from PCA of indoor VOC datasets.

In the loading plot (Fig. 4), compounds located toward a cluster direction contribute positively to the separation of the cluster along the corresponding score plot. Group I was characterized by decamethylcyclopentasiloxane (D5) as a major contributor (Fig. S2 (A)). Group II was characterized by toluene, ethyl acetate, and trichloroethylene (Fig. S2 (B–D)). Group III was situated near the origin of the PCA score space, with benzene partially contributing to its separation from other groups, selected as a representative compound based on confirmation with an authentic standard (Fig. S2 (E)). Meanwhile, other VOCs, such as aromatic and aliphatic hydrocarbons, were not further considered due to the lower confidence of their identification based solely on the NIST mass spectral library matching.

Fig. 5 shows the concentration changes in the TVOC (a) and individual VOCs (b–f) which were quantified by target analysis and characterized by PCA. The change in TVOC of each sample was observed within the range of 10–100 μg/m^3, despite its overall low concentrations (Fig. 5 (a)). D5 remained at low concentrations over a long period, with intermittent short-duration peaks observed during the hours when people were present in or near the room (DAY1_9-14, DAY5_8-13, DAY8_10-15, DAY11_8-13, DAY11_13-18) (Fig. 5 (b)). D5 has been reported to be attributable to the use of personal care products,[21] and the present results revealed a marked difference between occupied and unoccupied periods. Although Day 2 was a regular working day, no occupants were present near the sampling point. Therefore, the observed daytime increases in D5 could have been related to occupant-related activities. Toluene (Fig. 5 (c)) and ethyl acetate (Fig. 5 (d)) exhibited moderate variability, with multiple gradual increases and decreases over time. Trichloroethylene (Fig. 5 (e) and benzene (Fig. 5 (f)) showed temporal increases on Friday evening (Day2_20-1) and Saturday evening (Day3_16-21), respectively.

A comparison between conventional TVOC and the sum of concentrations of individual VOCs (D5, toluene, ethyl acetate, trichloroethylene, and benzene) characterized by PCA (PCA-derived TVOC) is shown in Fig. 6. Pearson correlation analysis using data from DAY1 to DAY12 showed a positive correlation ($r = 0.86$, $p < 0.001$). Meanwhile, the difference was observed, particularly on DAY11_8-13. The higher TIC peak areas of the sample were analyzed using the NIST mass spectral library, and dodecamethylpentasiloxane (L5) was identified as a major VOC, which was further confirmed by comparison with an authentic standard (Figs. S3, S4). L5 accounted for an increase of 14.6 μg/m^3 in the difference between the TVOC (82.9 μg/m^3) and the PCA-derived TVOC (30.5 μg/m^3) on DAY11_8-13. Although L5 was not identified as a major contributor in the PCA results (PC1 = 0.125, PC2 = 0.002 for L5), it was likely masked by the dominant influence of D5. The source of the L5 increase could not be identified in this study. Further measurements combined with detailed activity records are needed to clarify the factors contributing to increases in L5.

In the present study, the sampling time was set at 5 h for each time-segment to evaluate sequential temporal changes in VOC profiles over several days, including weekdays and weekends, while taking into account the sampling volume required to avoid breakthrough and the configuration of the sampling system. Although transient emission events can be averaged within 5 h sampling period, setting shorter sampling intervals can be applicable to the investigation of the emission sources.

Since outdoor air was not measured simultaneously in this

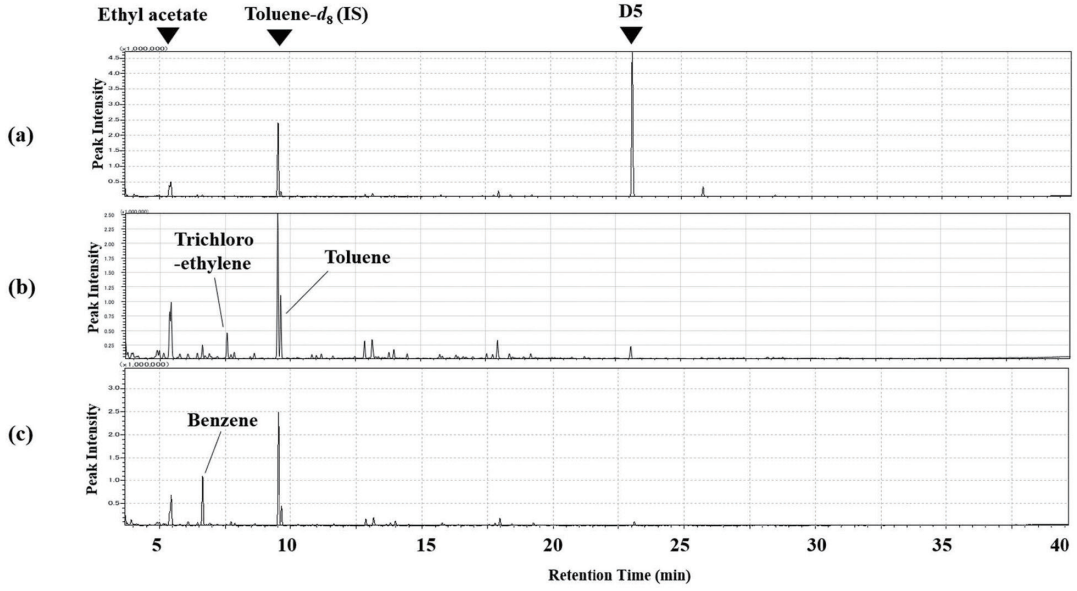

Fig. 2. Overview of Representative Total Ion Current (TIC) Chromatograms for Each Group

(a): Group I: DAY5_8-13, (B): Group II: DAY3_1-6, (C): Group III: DAY3_21-2. Toluene-d_8: Internal standard (IS). D5: Decamethylcyclopentasiloxane.

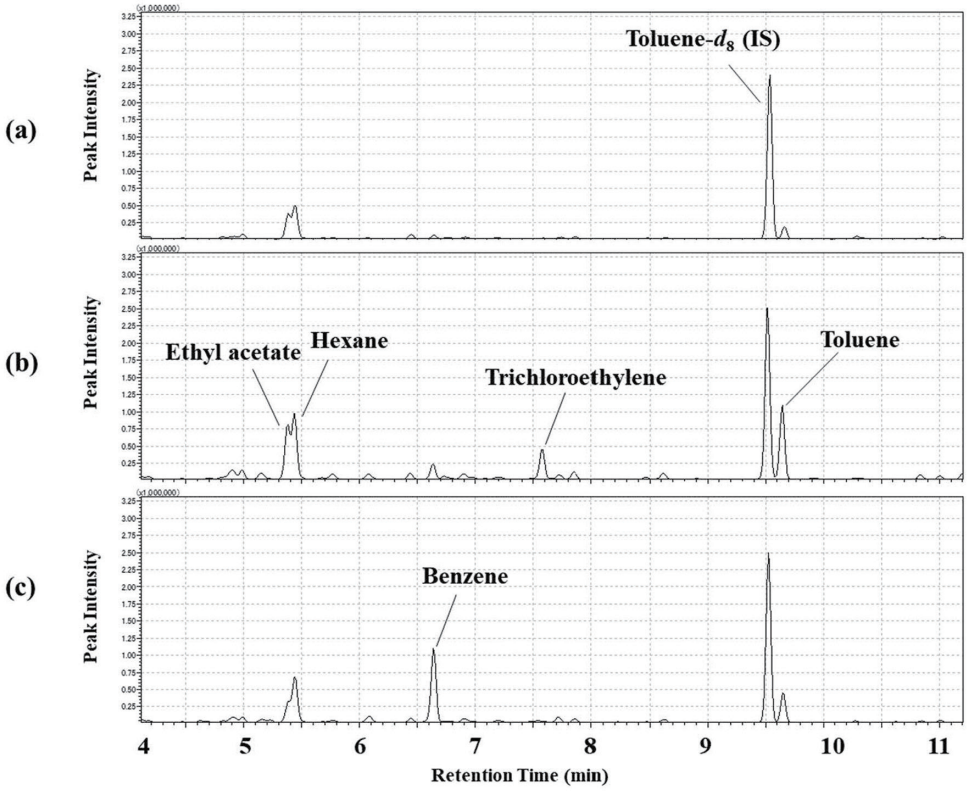

Fig. 2 (continued). Enlarged View of the Region Indicated in Fig. 2

study, the influence of outdoor air infiltration on the observed VOC variations cannot be completely excluded. However, the aim of this approach was not to separate indoor and outdoor contributions, but to explore changes in VOC profiles in indoor environment and to find candidate VOCs associated with gradual emission sources. Simultaneous outdoor measurements would be useful for clarifying the contribution of outdoor air to the observed VOC profiles in future studies.

It should be noted that PCA in the present study was performed using 468 VOCs as variables for 47 samples, meaning that the number of variables greatly exceeded that of samples. In high-dimensional data, the direction of principal compo-

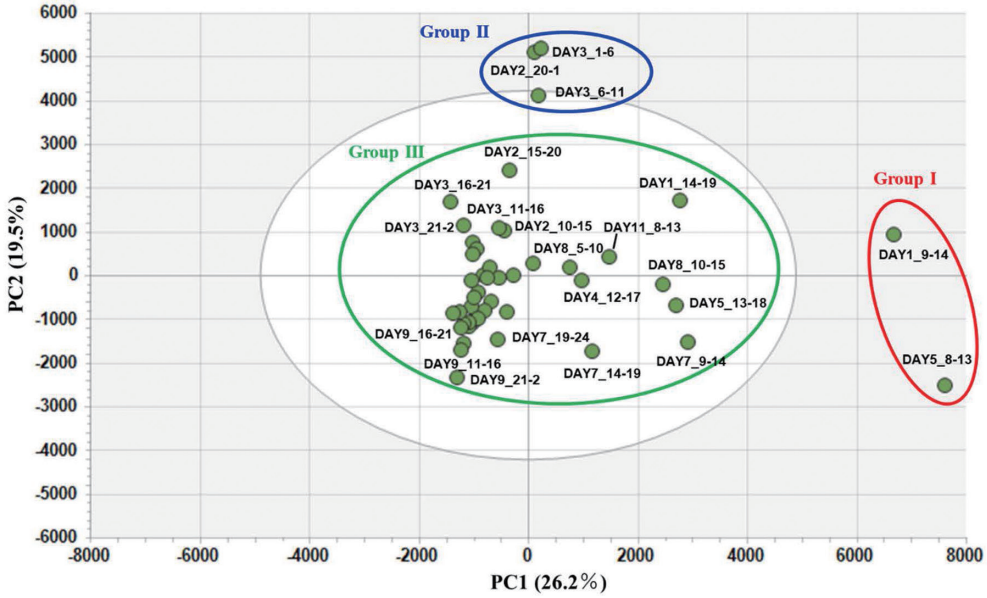

Fig. 3. PCA Score Plot of Indoor Air Samples for a Total of 10 Days by TD–GC–MS.
PC1 occupies 26.2% and PC2 19.5% of total variance.

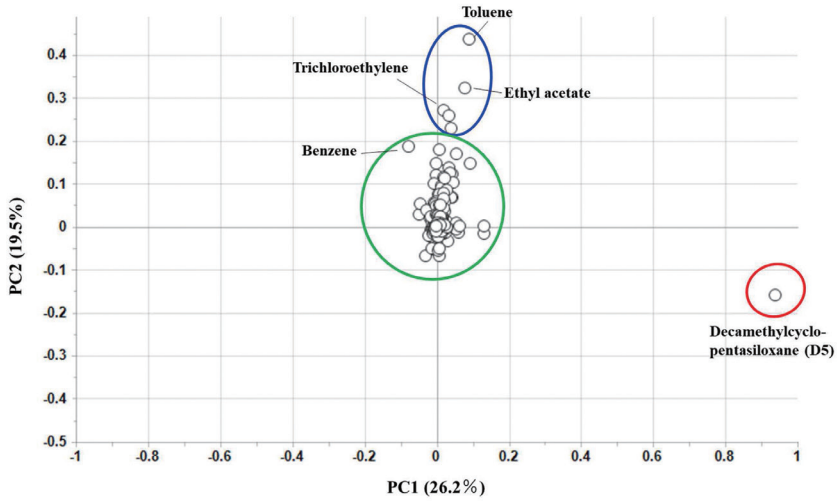

Fig. 4. PCA Loading Plot of Indoor Air Samples

nents and the interpretation of loadings may be sensitive to the characteristics of a small number of samples and to variable selection. Therefore, the groups observed in the PCA score plot should not be interpreted as fully validated classification, but rather as an exploratory summary of time-varying changes in indoor VOC profiles.

Targeted analysis is useful for accurately evaluating quantitative changes in specific VOCs. However, this approach does not readily provide a comprehensive understanding of simultaneous changes in multiple VOCs or similarities in temporal concentration profiles among samples. In contrast, application of PCA to temporal changes in indoor VOC profiles allows samples characteristic of specific time periods to be selected objectively and VOCs showing simultaneous changes to be identified efficiently. Therefore, applying PCA to sequential indoor VOC profiles can be useful for providing working hypotheses to identify candidate VOCs for subsequent investigation of time-varying emission sources.

Sequential sampling, TD–GC–MS analysis, and PCA are each a well-established technique. However, their combined application to indoor air study has been limited, particularly for non-target analysis of workplace air using sequential sampling. In contrast to conventional automated monitoring focused on a limited set of gaseous pollutants including nitrogen dioxide, our approach covers VOCs across the *n*-hexane– *n*-hexadecane volatility range and provides quantitative estimation of TVOC. In future studies, this approach will be directly extended from the present single-office-room case study under spring conditions to general residential houses to further evaluate its applicability under diverse real-life living conditions, including higher-temperature settings.

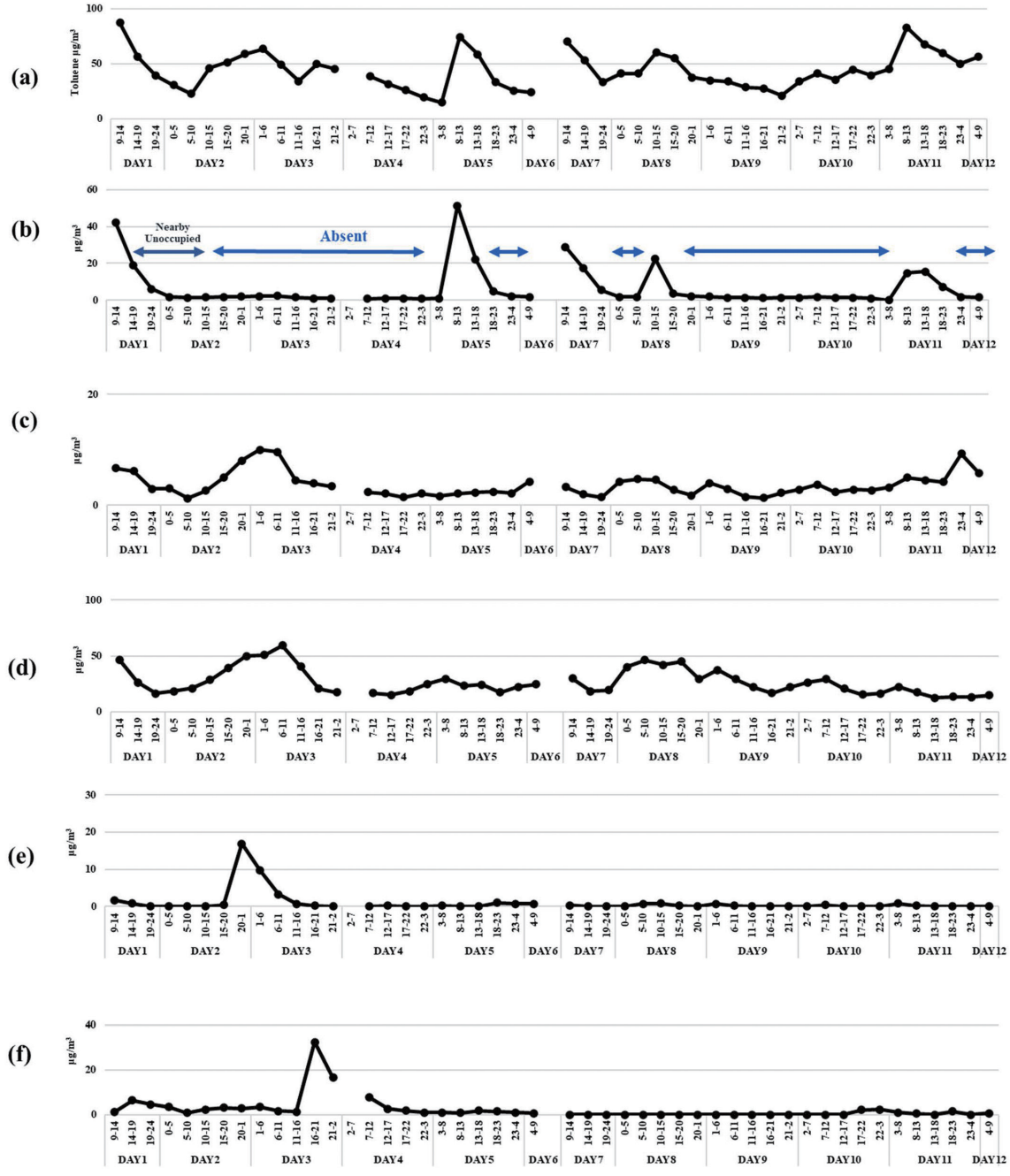

Fig. 5. Changes in Concentrations of TVOC and Individual VOCs.

(a): TVOC, (b): D5, (c): Toluene, (d): Ethyl acetate, (e): Trichloroethylene, (f): Benzene. DAY4_2-7 was missing due to low sampling volume.

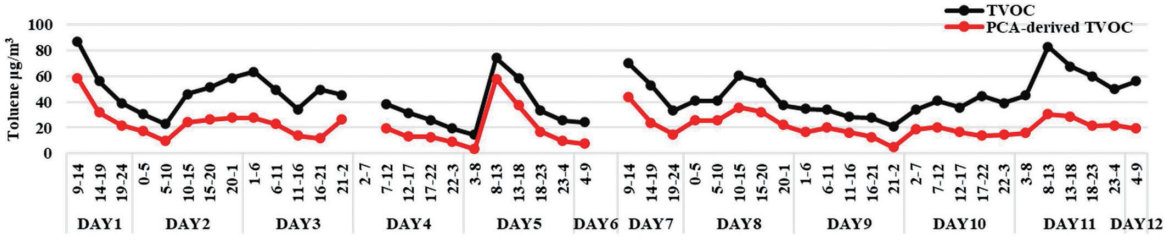

Fig. 6. Overlay View of Changes in Conventional TVOC and PCA-Derived TVOC (Sum of D5, Toluene, Ethyl Acetate, Trichloroethylene, and Benzene).

Pearson correlation between TVOC and PCA-derived TVOC: r = 0.86, $p < 0.001$, n = 47.

Conclusions Sequential indoor air sampling combined with multivariate analysis was applied to identify VOCs associated with gradual emission sources. PCA grouped the indoor air quality patterns. D5 exhibited intermittent increases during periods when occupants were present near the sampling point, whereas toluene and ethyl acetate showed gradual temporal variability. The VOCs identified by PCA contributed substantially to temporal increases in TVOC observed during the multi-day monitoring period. This approach can be useful for identifying VOCs from gradual emission events, associated with indoor air pollution.

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Conflict of interest The authors declare that they have no conflicts of interest.

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