



# Article Real-Time Phytoncide Monitoring in Forests: A Comparative Study of SIFT-MS and Conventional GC-MS Methods

Yeji Choi 🔍, Geonwoo Kim 🔍, Soojin Kim, Jae Hyoung Cho and Sujin Park \*🔍

Forest Human Service Division, Future Forest Strategy Department, National Institute of Forest Science, Seoul 02455, Republic of Korea; yeji6030@korea.kr (Y.C.); bkim5020@korea.kr (G.K.); kimsoojinsj@korea.kr (S.K.); cjh544@korea.kr (J.H.C.)

\* Correspondence: snowshoe@korea.kr; Tel.: +82-02-961-2862

Abstract: Conventional gas chromatography-mass spectrometry (GC-MS) analysis methods for measuring the concentration of phytoncides in forests are limited because of the need for an extended human presence in forests, the risk of errors, and contamination. To overcome these issues, this study introduces real-time measurement devices and selected ion flow tube mass spectrometry (SIFT-MS) as potential replacements. This study was conducted in the Hongneung Experimental Forest between 19 and 21 November 2019. A correlation analysis and independent samples t-test were performed to compare the GC-MS and SIFT-MS techniques. The diurnal patterns and trends in the phytoncide concentrations analyzed using the GC-MS and SIFT-MS methods were similar, suggesting the potential replacement of GC-MS with SIFT-MS. While both methods revealed similar major components in the daytime nonvolatile organic compounds (NVOCs), with pinenes comprising approximately half of the total percentage, the 24 h SIFT-MS analysis indicated reduced proportions of pinenes and benzaldehyde, along with the detection of more diverse NVOC compounds at night. Additionally, the studies indicated that GC-MS exhibited slightly higher selectivity, resulting in the detection of fewer NVOC compounds with SIFT-MS. The correlation analysis between the microclimate indicators and phytoncide measurement methods revealed differences: GC-MS with a mini pump showed positive correlations with fine dust and industrially derived VOCs, while the 24 h real-time measurements exhibited strong negative correlations. Consequently, while the GC-MS and SIFT-MS methods exhibited both similarities and differences in phytoncide concentrations, an independent samples *t*-test, confirming no statistically significant differences between the two methods, suggests the suitability of adopting SIFT-MS over GC-MS for phytoncide collection and analysis in forest environments. Nevertheless, this study contributes to the literature by comparing outdoor phytoncide levels using the GC-MS and SIFT-MS methodologies. These findings, which show that the methods are closely aligned, can guide future researchers in considering SIFT-MS equipment for phytoncide studies, offering a more accessible and efficient option with real-time capabilities.

Keywords: GC-MS; SIFT-MS; phytoncide; NVOC; VOC; real time

# 1. Introduction

Volatile organic compounds (VOCs) generate toxic substances, such as ozone, through photochemical reactions, which have been reported as the main causes of air pollution and global warming [1,2]. In urban areas, VOCs are mainly produced from emissions from factories and various transportation vehicles, and many countries are conducting policy efforts to reduce these emissions [3–5]. However, VOCs contain natural volatile organic compounds (NVOCs), which are released naturally from soil, wetlands, and forests. NVOCs are well-known phytoncides that are mixtures of several terpenes. Unlike many VOCs that cause air pollution, phytoncides improve human health [6–9]. The representative health-promoting effects of phytoncides include antibacterial and anti-inflammatory effects, stress reduction, depression relief, and aggressive tendency reduction [10]. In particular,



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). more than half of phytoncides are made up of alpha-pinene and beta-pinene, and these two substances have been found to be of significant help in anti-inflammation, sleep enhancement, and emotional stability, and as antioxidants [10]. Phytoncides also include other terpenes, such as limonene, camphene, and camphor, which are known to significantly improve both physiological and psychological health [6–10].

As the health promotion effects of phytoncides have been revealed through research, studies on phytoncides are being actively conducted in various countries, such as Korea, Japan, China, Germany, and the United States [6,10–15]. According to the results of previous studies, phytoncides have different emission characteristics depending on the species, and they occur more in coniferous forests than in broad-leaved forests [16–19]. In addition, it has been reported that a large amount is emitted in the summer rather than in the winter, and a large amount is discharged in early mornings and late evenings [14,19]. Phytoncides are also highly associated with the forest microclimate, which is known to be significantly affected by the forest light environment and has a strong correlation with temperature, humidity, and wind speed [14,19]. In addition, phytoncide emissions differ depending on the geographical characteristics, such as the location and altitude of the target site, and vegetation characteristics, such as forest stand age and density [20–22].

Therefore, various studies on phytoncides have been conducted worldwide. Most of the previous studies on phytoncides used an air collection mini pump to collect a sample in an adsorption tube and then derive the phytoncide concentration through a gas chromatography-mass spectrometry (GC-MS) analysis [19,23,24]. However, this analysis method takes more than a week to produce the final result, and the analysis unit price is very high, which makes it impractical in terms of research expenses. In addition, it is difficult to check the real-time concentration using the current survey method, and there is an error between the actual concentration and the analysis values owing to human intervention, low collection efficiency, and substance loss during the analysis process. In addition, phytoncide measurement using existing mini pumps requires a lot of manpower, as researchers must continue to reside in the forest and change the adsorption tube every hour. Therefore, effective phytoncide measurement and analysis measures are needed to increase the accuracy and precision of phytoncide concentrations in forest spaces and to reduce research personnel, costs, and time.

The GC-MS method was devised in the 1950s, and the selected ion flow tube mass spectrometry (SIFT-MS) method was introduced in the 1970s to compensate for its short-comings [25]. After several technical advances, the SIFT-MS method can now be used to measure and check for detected substances online in real time without human intervention. This dramatically reduces the time and manpower required for research and is mainly used in the medical and atmospheric engineering fields, such as for measuring the concentration of volatile metabolites in the blood or measuring indoor air quality. However, few studies have measured VOC concentrations in the atmosphere outdoors; in particular, no prior studies have measured phytoncide concentrations in the forest using the SIFT-MS method. Therefore, this study was conducted to develop a method to overcome the limitations of existing phytoncide measurement methods. Here, we statistically investigated whether a real-time measuring device and the SIFT-MS method could replace the existing air collection mini pump and GC-MS method.

#### 2. Materials and Methods

# 2.1. Study Site

This study was conducted in the Hongneung Experimental Forest located at the National Institute of Forest Science, Seoul, Republic of Korea (Figure 1a). The Hongneung Experimental Forest is also called the Hongneung Forest and Hongneung Arboretum. It was the first arboretum in Korea, built in 1922, and the first test site for modern forestry research with high historical, cultural, and academic value. The Hongneung Experimental Forest (37°35′45″ N and 127°02′37″ E) is located at the southwest foot of Cheonjangsan Mountain, east of Seoul, and 141 m above sea level. The Hongneung Experimental Forest

has an area of approximately 41.2 ha, of which 21.9 ha is a natural forest and 13.47 ha is an artificial forest with a total of 2035 plant species. In addition, there are eight gardens, including both natural and artificial forests. For this study, we measured phytoncides in Garden VIII, where coniferous and broad-leaved trees are mixed (Figure 1b). The main tree species in the eighth arboretum include *Tsuga sieboldii* Carriere, *Cotoneaster wilsonii* Nakai, *Ribes fasciculatum* var. *chinense* Maxim., and *Alangium platanifolium* var. *trilobum* (Miq.) Ohwi.



**Figure 1.** Images of the study site: (a) phytoncide-emission study sites in Seoul, Republic of Korea; (b) specific research area in the Hongneung Experimental Forest [26].

#### 2.2. Data Collection Methods

In this study, NVOC emissions and microclimate data were measured from 19 and 21 November in 2019. For the NVOCs and microclimate data, the experiments were conducted on three different plots within a radius of 10 m at each survey site to reduce measurement errors. Details on the NVOC and microclimate environmental data indicators measured in this study are shown in Table 1.

NVOCs		Microclimate Environment
Monoterpenes	cineole, 3-carene, camphene, camphor, cymene, borneol, fenchone, geraniol, limonene, menthol, myrcene, nerol, pinocarvone, pulegone, sabinene, sabinene hydrate, phellandrene, $\alpha$ -pinene, $\beta$ -pinene, $\alpha$ -terpinene, $\gamma$ -terpinene, terpinolene, terpineol	ground temperature, temperature, humidity, wind speed, maximum wind speed, fine-dust concentration level $(PM_{10}, PM_{2.5}, PM_{1.0})$ , industrial-derived volatile
Sesquiterpenes	caryophyllene, farnesene, guaiol, longifolene, nerolidol, valencene, $\alpha$ -bisabolol	concentration level ( $PM_{10}$ , $PM_{2.5}$ , $PM_{1.0}$ )
Nonterpenes	benzaldehyde, bornyl acetate, sabina ketone	,,

**Table 1.** Indicators for natural volatile organic compounds (NVOCs) and microclimate environment data that were measured for the study.

# 2.2.1. NVOCs through Mini Pump

NVOCs were gathered every two hours from morning (10:00) to afternoon (16:00) each day during the two-day research period, considering the peak times of forest visitation. Considering specific geographical features, NVOC measurements were conducted in three distinct circular plots situated within 5 m of the central tree. To accommodate the vegetation characteristics, six pumps were installed per plot. Samples were collected using the adsorption tube method, wherein the tubes contained 150 mg of Tenax TA (Markes International Inc., Sacramento, CA, USA). The NVOC levels were quantified in units of micrograms per cubic meter ( $\mu$ g/m<sup>3</sup>), with 'm<sup>3</sup>' representing the volume of the surrounding environment at the measurement locations. The total air volume of 9 L collected within an hour was converted to cubic m, as outlined below.

The sample collection system utilized a mini pump (MP-30KN; Sibata Scientific Technology Ltd., Saitama, Japan), and the calibration was performed by measuring the adsorption errors before using a flow meter. Overall, 9 L of NVOCs was collected at a flow rate of 150 mL/min. A previous study aimed at enhancing the precision and efficiency of NVOC measurements in forests investigated different sampling volumes and determined that 9 L yielded the most efficient results compared to 1, 3, 6, 9, 12, 24, and 48 L [27]. Consequently, the current study also adopted a 9 L air volume. The sampling apparatus was positioned on a tripod at a height of 1.5 m above the ground, and the process was repeated at each site to calculate the average value. Disposable polyethylene gloves and antibacterial masks were used during the experiment to prevent potential errors in contact with the tubes. The sampled tubes were stored at a temperature below 4 °C for 48 h after collection and prior to analysis (see Table 2). To minimize the chance of errors, data from tubes collected without Tenax TA inside were also considered.

Parameter	Conditions					
Column	HP-INNOWAX (60 m $\times$ 0.25 mm $\times$ 0.25 $\mu$ m, film thickness)					
Carrier gas flow	He at 1 mL/min					
Injection mode	Pulsed splitless					
Injection port temp.	210 °C					
Transfer line temp.	210 °C					
	Initial		Rate		Final	
Over temp. program	40 °C	3 min	8 °C/min	220 °C	3 min	40 °C
Post run	220 °C, 5 min					

Table 2. Conditions for the operating parameters for NVOC detection.

The samples were analyzed both qualitatively and quantitatively using a gas chromatography-mass spectrometer (7890N-5975; Agilent, Santa Clara, CA, USA) equipped with a thermal desorption device (GC-MSD; Gerstel TDS, Gerstel, Germany). In this system, the substances adsorbed onto the tube were concentrated in a low-temperature cryofocusing set-up that utilized high-purity helium gas drawn from a thermal desorption device at a rate of 1 mL/min. The system desorbed the gas for a duration of 3 min at 210 °C, maintaining a temperature of -30 °C. Subsequently, the compounds were subjected to a 3 min heating process at 220 °C before being injected into a GC spectrometer and detected by means of an MSD.

Several measures can be employed to validate analytical devices and procedures. One such measure involved the creation of a calibration curve using 20 different standard chemical species, which included  $\alpha$ -pinene and  $\beta$ -pinene. Utilizing this calibration curve to determine the mass number of each element and the square of its dilution rate with standard materials revealed that the majority of the materials exhibited a linearity exceeding 0.997. Noteworthy examples of this high linearity included  $\alpha$ -pinene (R<sup>2</sup> = 0.998), and d-limonene (R<sup>2</sup> = 0.999). The experiments involving these substances demonstrated a remarkable level of reproducibility in terms of the linear correlation coefficient, rendering them suitable for research purposes. Table 1 shows 32 target compounds quantified using standards and calibration curves.

# 2.2.2. NVOCs through Real-Time VOC Measurement Equipment

Phytoncide concentrations in the forest were measured in real time 24 h a day every 2 min from 19 November 2019 to 21 November 2019 using a SYFT Voice200 ULTRA Advanced SIFT Mass Spectrometer (Syft Technologies, Christchurch Central City, Christchurch, New Zealand). This is a SIFT-MS device that can directly qualitatively and quantitatively analyze the pptv level in real time without pretreatment of the samples, overcoming the difficulties of the gas chromatography-mass spectrometer (GC-MS) method, which is timeconsuming [25]. The SIFT-MS analysis method is as follows: Firstly, three types of reagent ions  $(H_3O^+, NO^+, and O_2^+)$  of the SIFT-MS are produced through microwave plasma energy using nitrogen, oxygen, and moisture in the atmosphere. The generated reactants are filtered through the first quadrupole mass filter and sequentially enter the flow tube. Secondly, the generated reagent ions are sequentially injected into the flow tube and stabilized by colliding with the cooling gas. The stabilized reagent ions encounter the sample and the ionization reaction proceeds. The flow rate, temperature, and pressure of the flow tube are kept constant, and the energy of the reagent ions is transferred to the sample to generate product ions. Lastly, the excess reagent ions that do not react with the generated product ions are filtered through a second quadrupole mass filter. The concentration of the sample can be immediately checked using the information of the compound stored in the Syft's compound library (collision constant, reaction speed constant, reaction rate, and other factors) [25,28,29]. Unlike previous GC-MS methods, it is possible to add a substance to be analyzed without a separate standard substance and to monitor concentration changes through an online system in real time. In addition, there is a difference in that it is easy to use by nonexperts because it has automatic validation and self-calibration functions.

# 2.2.3. Microclimate Environments

At each study site, the ground temperature, temperature, humidity, wind speed, and maximum wind speed were recorded to collect data on the microclimate environment variables. In addition, the directions and slopes of the sites were measured based on their locations. At five-minute intervals, the physical characteristics of the site's environment were monitored using a portable multifunction meter (HOBO-U23 V2; Onset Computer Corp., Bourne, MA, USA). Considering the geological features, a wind-monitoring sensor (Wind Monitor O5103-45; R. M. Young Company, Traverse City, MI, USA) was placed at each target site to collect wind velocity data. The meter was installed at a height of 1.5 m on a tripod, 5 m away from the mini pump, and digitalized measurement records were

saved and converted for the study. The results were analyzed using the HOBO-ware Pro software version 3.7.26 (Onset). To minimize the possibility of measurement errors, data saved 5 min before and after each measurement were omitted from the study.

Forest fine dust concentrations and industrially derived VOCs concentration data were also collected at the measurement site located in the Hongneung Experimental Forest. Data were collected using a fine dust measurement tower installed in the Hongneung Experimental Forest. Data were extracted using the online system of the Asian Initiative for Clean Air Networks (AICAN) operated by the National Institute of Forest Science in Korea [30]. The extracted concentration data included forest fine dust concentration levels ( $PM_{10}$ ,  $PM_{2.5}$ , and  $PM_{1.0}$ ) and industrial-derived VOCs concentration levels ( $PM_{10}$ ,  $PM_{2.5}$ , and  $PM_{1.0}$ ).

#### 2.3. Data Analysis Methods

In this study, the analysis was performed based on 24,219 raw data points collected using the equipment, with phytoncide concentrations collected with the mini pumps (GC-MS type) and real-time measurement equipment (SIFT-MS type), and the microclimate data with AICAN data. The analysis was performed using R 4.2.1, and the detailed analysis process is shown in Figure 2. Research was conducted to compare the data obtained with the mini pump, which has long been used in the field, with the data obtained with the newly applied real-time measuring instrument, and to confirm their accuracy. First, descriptive statistics, such as a comparison of the means and standard deviations of the two datasets, were performed. Following this, the correlation between the mini pump data and microclimate factors were analyzed. Subsequently, tests for normality and homogeneity of variance were performed, and an independent samples *t*-test was performed to determine the significance of the mean difference between the mini pump data and the real-time measured data.



Figure 2. Flow diagram of the analysis processes.

# 3. Results

# 3.1. Characteristics of NVOCs at Hongneung Experimental Forest

The NVOC emissions measured over time using a mini pump and real-time measuring instrument are shown in Figure 3. The red boxes in Figure 3 show the times when the mini pump and real-time measuring instrument were used simultaneously, and it can be seen that the increase and decrease tendencies were similar. As a result of comparing the average NVOC emissions from morning (10:00) to afternoon (16:00), measured using the two pieces of equipment at the same time, the average value measured using the mini pump was 1.790 µg/m<sup>3</sup>, and it was 2.963 µg/m<sup>3</sup> for the real-time measuring instrument, for phase 1. For phase 2, the average NVOC emissions value derived using the mini pump was 3.073 µg/m<sup>3</sup> and using the real-time meter was 4.035 µg/m<sup>3</sup>.



**Figure 3.** NVOC emissions graph using the real-time and measurement equipment. Phase 1: average NVOC emissions from morning to afternoon on 19 September 2019. Phase 2: average NVOC emissions from morning to afternoon on 21 September 2019.

The detailed components of the NVOC concentrations, measured using a mini pump and real-time measuring instrument, were examined. Owing to the classification of the detection items in the real-time measuring instruments, alpha-pinene, beta-pinene, and 3-carene were detected integrally, and alpha-terpinene and gamma-terpinene were also detected integrally. Accordingly, the measured values of the mini pump were grouped to compare the materials of the two devices. A total of 20 types of phytoncides were detected in the daytime measurements using mini pumps, and pinenes (45.5%) accounted for approximately half (Figure 4a). Benzaldehyde (20.2%), camphene (6.50%), limonene (5.11%), and myrcene (4.83%) were detected in high concentrations. In the measurements using a real-time device during the daytime, 10 types of NVOCs were detected. Pinenes (50.3%) accounted for approximately half of the total (Figure 4b), followed by benzaldehyde (26.9%), camphene (9.0%), limonene (4.8%), and myrcene (4.5%). In addition, 13 phytoncides were detected in the real-time data measured for 24 h, followed by benzaldehyde (16.9%), pinenes (14.9%), terpinenes (12.5%), terpinolene (11.5%), and bornyl acetate (9.5%) (Figure 5). High concentrations of pinenes and benzaldehyde were found in both types of equipment during the daytime.



**Figure 4.** Detailed components of NVOCs concentration: (**a**) percentage of the detailed components of the daytime NVOC emissions extracted using the mini pump; (**b**) percentage of the detailed components of the daytime NVOC emissions extracted using the real-time measuring equipment.



**Figure 5.** Percentage of the detailed components of the 24 h NVOC emissions extracted using real-time measuring equipment.

# 3.2. Correlation Analysis of NVOCs and Microclimate Environments

Several previous studies have shown that phytoncide emissions have a strong correlation with microclimatic factors, such as temperature and humidity. Accordingly, in this study, a Pearson's correlation coefficient analysis was performed to confirm that both measurement methods had the same tendencies as in previous studies. In the case of the mini pump, because it was measured four times a day for two hours with six equipment units, microclimate factor data were also extracted according to the mini pump measurement time and analyzed based on 48 datasets. In the case of the real-time measuring instruments, 48 datasets were analyzed according to the microclimate factor data measured in hourly units.

According to the analysis results, when daytime (10:00–16:00) phytoncides were measured with a mini pump that had been used in the past, the same correlation tendency with microclimate factors as in previous studies could be observed (Figure 6a). There was a significant positive correlation with temperature and a significant negative correlation with wind speed. Although there was no significant correlation with humidity, there was a weak negative correlation. Fine dust and industrially derived VOCs generally had a positive correlation, and at the  $PM_{10}$  level, all had a significant correlation. In the case of real-time daytime phytoncide measurements, similar to previous studies and conventional mini pump methods, there was a positive correlation with temperature and negative correlations with humidity and wind speed (Figure 6b). There was no significant correlation between fine dust and industrial-derived VOCs. However, in the phytoncide measurements over 24 h using a real-time measuring device, similar to the results of previous studies, it was also found that there was a strong positive correlation with ground temperature and temperature and a strong negative correlation with humidity. Although there was no significant correlation with wind speed and maximum wind speed, a weak negative correlation was confirmed. However, unlike the measurement results obtained using a mini pump, a strong negative correlation was observed between fine dust and industrially derived VOC (Figure 7).



**Figure 6.** Results of the Pearson correlation coefficient analyses: (**a**) correlation between daytime NVOCs concentration measured using the mini pump and microclimate indicators; (**b**) correlation between the daytime NVOCs concentration measured with the real-time measurement equipment and microclimate indicators. The red box highlights the correlation between each measurement technique and the microclimate environment. \* p < 0.05, \*\* p < 0.01, \*\*\* p < 0.001.



**Figure 7.** Correlation between the 24 h NVOCs concentration measured using the real-time measurement equipment and microclimate indicators. The red box highlights the correlation between the measurement technique and the microclimate environment. \* p < 0.05, \*\* p < 0.01, \*\*\* p < 0.001.

# 3.3. Independent Samples t-Test for NVOCs Measurement Results

An independent samples *t*-test was performed to confirm whether there was a significant difference between the NVOC concentrations measured using a mini pump and the NVOC concentrations measured using a real-time measuring device. Before performing the independent samples *t*-test, the Shapiro–Wilk normality test and Levene's test for homogeneity of variance were performed. The results of the normality test showed that the *p*-value was greater than 0.05 for both the mini pump and the real-time measuring instrument, satisfying the assumption of normality of the two groups. The results of the homogeneity of variance test showed that the *p*-value was 0.976, confirming that the variance between the two groups was the same. Accordingly, an independent samples *t*-test was performed on the two groups, and the detailed results are shown in Table 3. According to the results, the *p*-value was 0.513, confirming that the difference in the mean between the two groups was not statistically significant. This indicates that the measured NVOC concentrations in the two groups were not significantly different.

**Table 3.** Results of an independent samples *t*-test undertaken on the data measured using a mini pump and that using a real-time measuring instrument.

Shapiro-Wilk Normality TestLevene's Test for Homogeneity of Variancet-Test for Equality of Mean (Equal Variance Assumed)p-Valuep-ValueFp-ValueMean DifferenceSE95% Confidence Interval of the DifferenceMini Pump TimeReal PumpFp-ValueDfp-ValueMean DifferenceSE Difference95% Confidence Interval of the Difference	Independent Samples <i>t</i> -Test										
<i>p</i> -Value <u>F</u> <i>p</i> -Value t Df <i>p</i> -Value Mean SE Difference Difference Difference Lower Upper	Shapiro–WilkLevene's Test for Homogeneity of Variancet-Test for Equality of M			ity of Mean (Ec	qual Variance A	ssumed)					
Mini Real Pump Time Lower Upper	<i>p</i> -Value		- F	<i>p</i> -Value	t	Df	<i>p</i> -Value	Mean	SE	95% Confidence Interval of the Difference	
	Mini Pump	Real Time		F	. D	DI		Difference	Difference	Lower	Upper
0.512  0.630  0.467  0.976  -0.656  174  0.513  0.471  0.128  -0.354  0.178	0.512	0.630	0.467	0.976	-0.656	174	0.513	0.471	0.128	-0.354	0.178

Df: degrees of freedom; SE: standard error.

#### 4. Discussion

As phytoncides emitted by plants have been proven to have beneficial effects on human health, many studies have been conducted worldwide. Studies are also being conducted to measure NVOC concentrations directly in forests; however, GC-MS analysis methods, which were mainly used in the past, have several limitations. With this method, human intervention is required, such as the researcher staying in the forest for a relatively long period and changing the collection tube; therefore, this method is always exposed to the risk of human error and sample contamination. In addition, GC-MS analysis is expensive and time-consuming and requires expert knowledge to handle the equipment. Therefore, this study introduced and analyzed real-time measuring instruments and SIFT-MS analysis methods in an indoor environment on a trial basis with the aim of deriving new methods that can replace existing phytoncide collection and analyzed the concentration level using the SIFT-MS method within a minute. Although many previous VOC-related studies have been conducted comparing the existing GC-MS method with the SIFT-MS method, most of them measured VOC concentrations indoors or in the laboratory, and there is no study measuring phytoncides outdoors, especially in the forest [31,32]. Therefore, in this study, phytoncide concentrations in the forest were measured using both GC-MS and SIFT-MS methods.

As a result, the concentration of phytoncides analyzed using the GC-MS method and the concentration analyzed using the SIFT-MS method showed similar diurnal patterns and increased and decreased tendencies. This positive result indicated the possibility of replacing the existing GC-MS method with SIFT-MS. However, the concentration of phytoncides obtained using SIFT-MS was slightly higher than that obtained using the GC-MS method, which may be due to volatilization and contamination during the sampling, transport, and analysis processes owing to the need for human intervention in the GC-MS method. In addition, more phytoncide compounds may have been collected using SIFT-MS, which can detect phytoncide concentrations without being affected by moisture, as deep forests are mostly shaded and always moist.

In addition, the detailed composition and ratio of phytoncides revealed similarities and differences between the two methods. Regarding the detailed composition of daytime NVOCs, the GC-MS and SIFT-MS methods both presented results similar to those of previous studies; pinenes accounted for approximately half of the total percentage. This was followed by benzaldehyde, camphene, limonene, and myrcene. However, the results of the 24 h SIFT-MS analysis showed that benzaldehyde, pinenes, terpenes, and terpinolene were similar at approximately 15% each [33–35]. Compared to daytime measurements, this indicates that the proportion of pinenes and benzaldehyde was reduced and more diverse NVOCs were detected in the 24 h results, which included the nighttime data. In addition, 20 types of NVOCs were detected with the GC-MS, whereas the SIFT-MS detected only 10 types during the daytime and 14 types throughout the day. In both methods, the major components were similar during the daytime; however, even though the study was conducted at the same site, the composition ratio and the detection material differed over time, probably because of the measurement time or variation in tree species. Most of the trees at the measurement site were pine species. Therefore, pinenes emitted mainly from pine trees may have been detected at their highest levels during the daytime measurements [36–38]. In addition, the difference in the constituent materials between the daytime data and the 24 h data may be due to the photochemical reactivity of the phytoncide. Volatile organic compounds, including phytoncides, disappear in response to solar radiation and form ozone [39,40]. Therefore, in places or times when sunlight is strong, greater amounts and types of phytoncides disappear before being detected by the equipment. Therefore, it can be assumed that the phytoncide compounds that did not emerge during the day were found in the 24 h measurement results because light-sensitive phytoncide compounds were volatilized during the day with strong sunlight and detected at night with less light impact.

In addition, previous studies have shown that GC-MS has slightly greater selectivity for analyte identification than SIFT-MS. Therefore, fewer NVOCs may be detected with SIFT-MS than with GC-MS [41].

Differences were also observed in the results of the correlation analysis between the microclimate indicators and the two phytoncide measurement methods. In the case of the GC-MS method using a mini pump, it was found that both fine dust and industrially derived VOCs had a positive correlation, while the 24 h real-time measurements had a strong negative correlation with both fine dust and industrially derived VOCs. It can also be assumed that this is influenced by the measurement time. The soil temperature decreases before the air temperature at night, stabilizing the air and causing air pollutants to sink near the surface [42]. In this study, the equipment was installed relatively close to the surface at a height of 1.5 m. Previous studies have shown that phytoncide emissions also decrease owing to reduced plant activity at night and other environmental factors [19]. However, owing to atmospheric stabilization, fine dust and industrial-derived VOCs, such as automobile smoke, may have accumulated on the surface during the night, raising their concentration. In contrast, in the case of mini pumps, fine dust and pollutants tended to decrease when phytoncides decreased. The decrease in phytoncide levels during the day could be due to rain and strong wind speeds. The average humidity during the daytime (10:00–16:00) at the time of measurement was 36.8%, and the average humidity at other times was 49.9%, indicating that it was not due to rain. When comparing the average wind speed, the average wind speed during the day was 1.9 m/s, and at other times it was 0.4 m/s, indicating the possible influence of the wind speed. A relatively stronger wind speed during the day than during the nondaytime may have caused other VOC materials to decrease when the phytoncide concentration decreased. However, in the case of the real-time measurement devices, the results were possibly different because the phytoncide concentrations were collected at other times when the wind speed was relatively weak, as well as during the day, and the atmospheric characteristics at night were reflected.

As such, there were similarities and differences between the phytoncide concentrations analyzed using the GC-MS and SIFT-MS methods. Therefore, in this study, an independent samples *t*-test was performed to determine whether the difference between the two analysis methods was statistically significant. Both groups satisfied the assumptions of normality and homogeneity of variance; therefore, an independent samples *t*-test was performed. There were no statistically significant differences in the means between the two groups. This indicates that there was no significant difference between the results obtained using the GC-MS and SIFT-MS methods. Therefore, when collecting and analyzing phytoncides in a forest, SIFT-MS can be adopted instead of GC-MS.

Based on these results, it is possible to introduce SIFT-MS for forest phytoncide measurements and apply it in the field. However, there are several limitations of this study; therefore, it is necessary to consider these in field applications. The biggest limitation of this study was the difference in the measurement time between the two methods. As mentioned earlier, real-time measuring devices measure 24 h a day, while mini pumps measure only during the day; therefore, external factors such as tree physiology and microclimate environment may have affected the two datasets. In addition, this study was conducted over a relatively short period of time of two days; therefore, there was a limit to collecting various data. Therefore, in subsequent studies, it is desirable to collect phytoncides 24 h a day for both mini pumps and real-time measuring instruments during sufficient research periods to reflect various external factors. In addition, because phytoncide-related studies deal with several compounds not covered by the overall VOCs research, it is necessary to reconfirm the accuracy of the SIFT-MS method, which does not directly draw calibration curves using standard materials. Lastly, because this study was conducted on a clear day, it would be a meaningful follow-up study to compare the phytoncide concentration on humid or rainy days using the GC-MS method by utilizing the characteristics of SIFT-MS that are less affected by humidity.

Nevertheless, this study is meaningful because it measured and compared the concentration of NVOCs outdoors, particularly in deep forests, using both the GC-MS and SIFT-MS methods. It is certainly not easy for researchers to collect phytoncide outdoors through a mini pump over a long period and analyze the value through a GC-MS method which requires a lot of effort. SIFT-MS is an attractive device for researchers studying phytoncides because it is easier to analyze, faster than GC-MS, and allows researchers to check phytoncide concentration values online and in real time at home or in laboratories. Therefore, the results of this study, which found that there was no significant difference in the results of the SIFT-MS and GC-MS and that both pieces of equipment generally had similar tendencies, can be used as a basis for researchers' decision making regarding the introduction of SIFT-MS equipment in the future.

# 5. Conclusions

Numerous studies worldwide have been conducted to explore the health benefits of phytoncides emitted by plants. The measurement of phytoncides is often hindered by the limitations of the traditional GC-MS analysis methods that requires a prolonged human presence in forests, leading to potential errors and contamination. This study sought to introduce and test real-time measuring instruments and SIFT-MS analysis techniques as potential replacements for existing phytoncide measurement methods. The results show that both GC-MS and SIFT-MS demonstrated similar diurnal patterns and trends in phytoncide concentrations, suggesting the potential of SIFT-MS to replace GC-MS. Additionally, both methods revealed similar major components in daytime nonvolatile organic compounds (NVOCs). The statistical analysis showed no significant disparities between the two methods, implying the feasibility of adopting SIFT-MS for forest phytoncide measurements. Therefore, this study is significant because a comparative analysis of outdoor concentrations of NVOCs was conducted, particularly in dense forest environments, using both the GC-MS and SIFT-MS methodologies. The disparity between the outcomes obtained using the SIFT-MS and GC-MS techniques were neither substantial nor significant and, overall, were congruent. This research offers valuable insight for researchers, suggesting the potential adoption of SIFT-MS equipment in future investigations.

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