*Research article*

# Potential Estimation of Secondary Pollutant Formation of BVOC from *Peltophorum pterocarpum* in Urban Area

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## Abstract

**Keywords**

Biogenic volatile organic compound (BVOC);

Secondary organic aerosol potential (SOAP);

Ozone formation potential (OFP);

*Peltophorum pterocarpum*;

urban area

Climate change affects the emission of biogenic volatile organic compounds (BVOCs) from plants, especially isoprene, α-pinene, and β-pinene. These compounds play vital role in the secondary organic aerosol potential (SOAP) and ozone formation potential (OFP) through photochemical reactions. In Thailand, daytime temperatures typically reach up to 40°C resulting in potential plant stress. The considered plant *Peltophorum pterocarpum*, emits high levels of BVOCs and is widely cultivated in the urban areas of Bangkok. Consequently, this research aimed to study the variations in BVOC concentration, SOAP, and OFP associated with *Peltophorum pterocarpum*, during the daytime. The BVOCs (isoprene, α – pinene, and β – pinene) were sampled using a dynamic enclosure system from 9:00 to 11:00 local time and analyzed using gas chromatography with a flame ionization detector. SOAP and OFP were estimated using fractional aerosol coefficient and maximum incremental reactivity. The results revealed an average BVOC concentration of 4.68 $\mu g/m^3$, which depended on temperature and light intensity. The highest SOAP and OFP were 1,367.10 and 188.58 $\mu g/m^3$, respectively, which were largely influenced by β – piene. This study aids in understanding the role of secondary pollutant formation involving BVOCs emitted from trees in urban areas, which can lead to the selection of low BVOC-emitting tree species and improvement of guidelines for planning urban forest areas.

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## 1. Introduction

Air pollution has become an important environmental issue in Thailand, affecting human health, economy, and society. Bangkok is Thailand's capital and it includes urban areas in which high levels of polluted volatile organic compounds (VOCs), nitrogen oxides (NO + $NO_2$), particulate matter less than 2.5 micron ($PM_{2.5}$), and sulfur oxides ($SO_x$) regularly occur. Moreover, emerging secondary pollutions such as ground level ozone ($O_3$) have become a serious issue especially [1, 2]. Secondary organic aerosols (SOAs) also play a role in the atmospheric reactions in urban areas. These derived pollutants have a stronger impact on the Earth's radiative balance, air quality, and human health than that of primary pollutants [3-5]. The Thai government has developed urban green areas to reduce urban air pollution. $O_3$ and SOA can be produced from both BVOC and anthropogenic volatile organic compounds (AVOCs), which were oxidized by hydroxyl radicals (•OH) [6 - 9], $O_3$, or nitrate radicals ($NO_3$•) in the ambient air [10-12]. The primary sources of VOCs are biogenic with plants contributing about approximately 65%, while anthropogenic sources contribute 25%, and wildfires contribute only 10%. Plants generally emit BVOCs such as isoprene, α – pinene, and β – pinene which play a role in growth regulation, plant reproduction, and signal and protective mechanism against stress [13, 14]. However, plants in urban areas are often stressed by the diurnal impact of temperature, heat [15] and light intensity from the urban heat island (UHI) effect. BVOC was not only the highest emission source of VOCs, but its chemical reactivity with •OH, $O_3$, and $NO_3$• was also higher than that of AVOCs [16]. Isoprene, α – pinene, and β – pinene are the dominant gases emitted from plants which react with •OH, •$NO_3$, and are transformed to $O_3$ and SOA during the daytime [17, 18]. The transformations are shown in equations (1)-(4):

$$\text{BVOC} + \bullet\text{OH} \rightarrow \text{RO}_2\bullet \quad (1)$$

$$\text{RO}_2\bullet + \text{NO} \rightarrow \text{NO}_2 + \text{RO}\bullet \quad (2)$$

$$\text{NO}_2 + h\nu\ (<420\ \text{nm}) \rightarrow \text{NO} + \text{O} \quad (3)$$

$$\text{O}_2 + \text{O} \rightarrow \text{O}_3 \quad (4)$$

In summer, temperatures in Thailand can reach up to 40°C during the daytime. The higher temperature induces plant stress, resulting in higher emission of isoprene, α-pinene, and β-pinene. *Peltophorum pterocarpum* is a tree species widely grown in Bangkok. This species emits high BVOCs, especially isoprene and monoterpenes (α – pinene and β – pinene) [19]. Thus, *Peltophorum pterocarpum* in urban areas are unavoidably affected by stressful conditions. Many studies have reported experiments on $O_3$ and SOA formation, but there are still some gaps in the exploration of $O_3$ and SOA formation. Therefore, ozone formation potential (OFP) and secondary organic aerosol potential (SOAP) were used to estimate the transformation to secondary pollutants [20, 21]. This study aimed to estimate the $O_3$ and SOA formation potential of *Peltophorum pterocarpum* in urban areas. These results contribute to understanding the role of secondary pollutant formation in urban areas, leading to the selection of low BVOC emission tree species, and the development of improved guidelines for planting urban forests.

## 2. Materials and Methods

### 2.1 Study area and plant selection

Kasetsart University is situated in an urban area in Bangkok (13°50′54.95″N 100°34′04.98″E). *Peltophorum pterocarpum* is one of the most abundant plant species in this area, with approximately 310 trees per $1.36 \times 10^6$ square meter. These trees are typically planted along the streets and within Warunawan Park University (Figure 1). Thailand's average annual temperature in 2020 was 26°C but in summer the highest temperature was 40°C. *Peltophorum pterocarpum* is the most common cultivated species in Southeast Asia and ranks high among plants for BVOC emission. *Peltophorum pterocarpum* has a rounded canopy and can reach a height of 15 m with a 30-50 ft spread; its leaves are bipinnate and 9-18 cm long. Samples of BVOCs were collected from *Peltophorum pterocarpum* on selected dates in summer (April and May 2022) during the daytime (9:00-11:00 local time). The sampling branch was the healthiest one that complied with the following criteria: it needed to receive full sunlight, be free from diseases, be well-developed, and have no other biotic and abiotic stress sources [22].

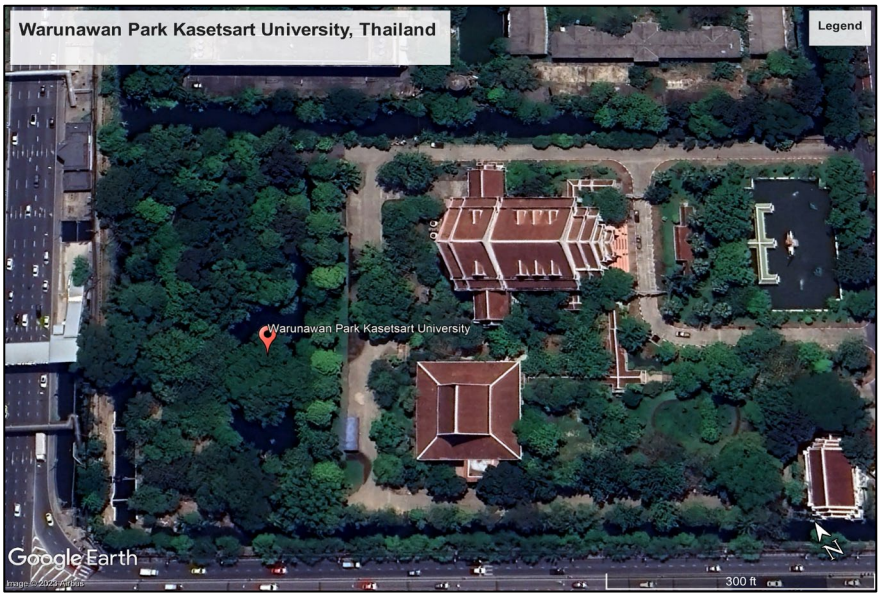


**Figure 1.** Study area: Warunawan Park, Kasetsart University, Thailand

### 2.2 BVOC sampling and analytic methods

This study used a dynamic enclosure system [23], as shown in Figure 2. The dynamic system included four major parts namely, 1) BVOC enclosure bag (HEDETECH, Tedlar bag, 25 L, DuPont, USA), 2) BVOC sampling bag (HEDETECH, Teflon bag, 10 L, DuPont, USA), 3) temperature and light intensity measurement system with Thermo-Hygrometer (EAE Technology, Oria Thermostat PM R1.0, Istanbul, Turkey), and a quantum sensor (Apogee Instruments, models SQ-100 series quantum sensors, Utah, USA), respectively, and 4) VOCs analyzer with a gas chromatography flame ionization detector (GC–FID). The average leaf area of samples was 0.16 m², which was determined

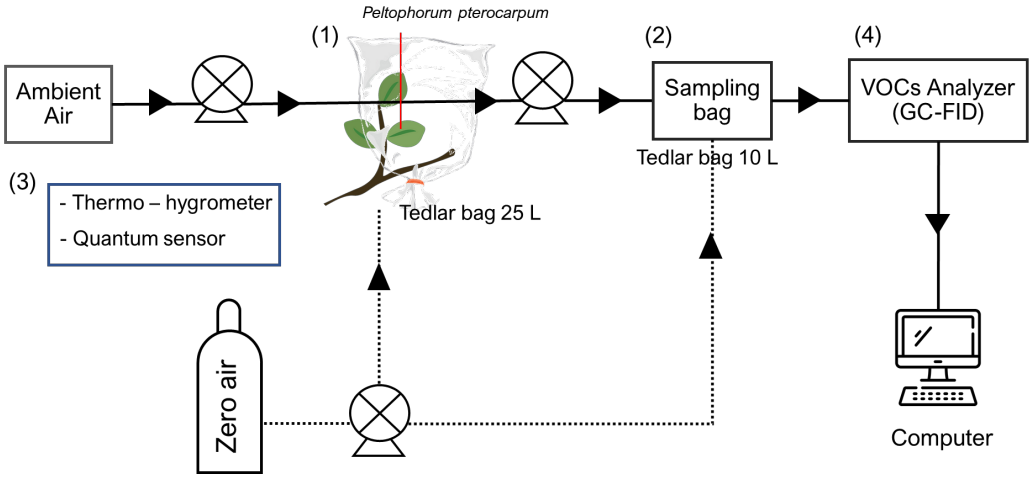


**Figure 2**. Schematic diagram of BVOC sampling from the *Peltophorum pterocarpum*

by Image J program version 1.53e. The leaves were later covered by BVOC enclosure bag and sealed with a cable tie. Ambient air was added to the BVOC enclosure bag using a vacuum pump at a flow rate of 5.0 L/min. The samples were collected from three positions on the same branch that had the same environmental conditions for shade, light intensity, temperature, and relative humidity (total samples were 21 samples). After 2 h (09:00-11:00 LT), each sample was collected into a sampling bag using a pump at a flow rate of 5.0 L/min. BVOCs were analyzed using a VOCs analyzer with a gas chromatography flame ionization detector (GC–FID). The BVOC enclosure bag was cleaned with zero air to remove the previous volatile organic compound before the next analysis, and the background was collected into an empty enclosure bag without the branch, as shown in Figure 2. BVOCs were continuously measured every 30 min using the VOCs analyzer, as shown in Figure 2. A thermoelectric cooling system was used to maintain temperatures below the evaporation point. The VOCs analyzer was calibrated prior to use using mixed VOC standard gases ($R^2 = 0.99$). Isoprene was measured using an A11000 airmoVOCs C2–C6 analyzer, while α-pinene and β-pinene were measured using an A21022 airmoVOCs C6–C12 analyzer. The VOC measurements were reported using Vistachrom software (version 1.4.6 b.).

## 2.3 Environmental conditions

Environmental parameters, particularly light intensity, temperature, and relative humidity affect BVOC concentration. Therefore, during the sampling period, these parameters were also measured. The light intensity of photosynthetically active radiation (PAR) was measured using a quantum sensor (Model SQ-100) and expressed as photosynthetic photon flux density (PPFD). Temperature was measured using a thermo-hygrometer located beside the sampling area, as shown in Figure 2.

## 2.4 SOAP and OFP estimation

The estimate of SOAs from isoprene, α – piene, and β – piene was calculated as secondary organic aerosol potential (SOAP) based on the fractional aerosol coefficient (aerosol formation coefficient (FACi) for isoprene, α-pinene, and β-pinene, which were 2, 30, and 30, respectively [24]. Equation (5) showed the SOAP estimates.

$$SOAP_i = [VOC]_i \times FAC_i \quad (5)$$

$SOAP_i$ = Amount of SOA generated by VOC for species i ($\mu$g/m$^3$)
$[VOC]_i$ = Initial mass concentration of VOC for species i ($\mu$g/m$^3$)
$FAC_i$ = aerosol formation coefficient of the VOC species i

Ozone formation from VOCs was studied using different methods; however, the ozone formation potential (OFP) was usually used to estimate the contribution of $O_3$ from VOCs [25-27]. The estimated $O_3$ formation was calculated from the maximum incremental reactivity (MIR). The MIR values of isoprene, α – piene, and β – piene were 10.61, 4.51, and 3.52 gVOC/g $O_3$, respectively [28]), which were derived in scenarios where the $NO_x$ had been adjusted to yield the highest incremental reactivities of VOCs, and OFP was calculated using equation (6):

$$OFP_i = [VOC]_i \times MIR_i \quad (6)$$

$OFP_i$ = Ozone formation potential for species i ($\mu$g/m$^3$)
$[VOC]_i$ = Concentration of $VOC_i$ for species i ($\mu$g/m$^3$)
$MIR_i$ = Maximum incremental reactivity of species i (g VOC/g $O_3$)

## 3. Results and Discussion

### 3.1 Biogenic volatiles organic compound concentration

BVOCs included isoprene, α-pinene, and β-pinene concentrations from *Peltophorum pterocarpum* with corresponding temperatures and light intensities, as shown in Figure 3. These results indicated that TBVOC concentrations increased with temperature and light intensity. The average concentrations of isoprene, α-pinene, and β-pinene were 0.70, 1.82, and 11.52 $\mu$g/m³, respectively. The averaged light intensity, temperature, and relative humidity were 127.06 $\mu$mol/m²s, 29°C, and 74.21%, respectively. The highest isoprene, α-pinene, and β-pinene emissions of 2.40±0.12, 3.27±0.16, and 42.14±2.11 $\mu$g/m³ were observed on 27$^{th}$ April. Light intensity affects photosynthesis in *Peltophorum pterocarpum*, influencing activity in the secondary metabolic process to respond to abiotic stress, resulting in the production and emission of more BVOC [28]. According to Zervoudakis *et al*. [29], plants which were exposed to 25% of full sunlight on a sunny day exhibited photosynthetic activity levels less than those exposed to 50%, 75%, and 100% of full sunlight (1,400 $\mu$mol/m²s), resulting in less BVOC production. Temperature is another significant factor affecting the release of isoprene, α-pinene, and β-pinene [30]. Increased temperature affects stomatal opening resulted in releasing more VOCs [31, 32]. Furthermore, *Peltophorum pterocarpum* possesses glandular trichomes capable of synthesizing and accumulating BVOC on the leaf surface, which are promptly emitted in response to abiotic stress conditions such as variations in light intensity and temperature [33].

### 3.2 SOAP and OFP estimations

#### 3.2.1 SOAP estimation

The SOAP of isoprene, β – piene, and α – piene emission from *Peltophorum pterocarpum* in urban areas are shown in Table 1. The average of SOAP of isoprene, α – piene, and β – piene were 1.40,

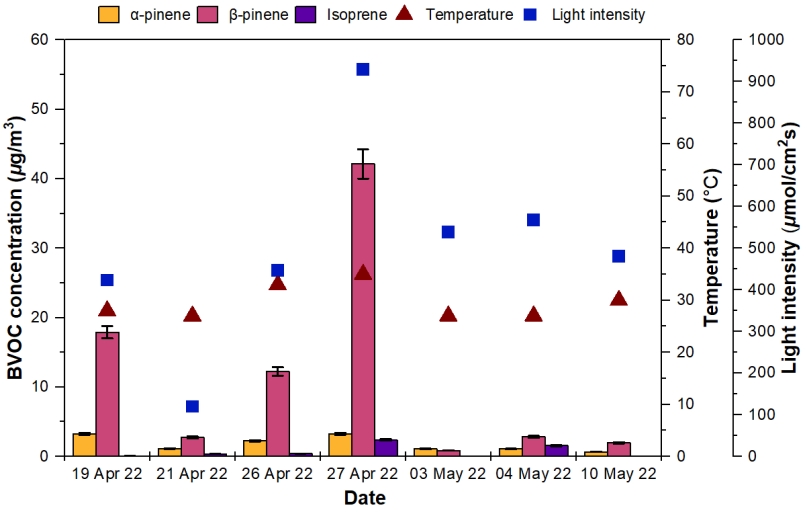


**Figure 3.** BVOC concentrations from *Peltophorum pterocarpum* in Warunawan Park, Kasetsart University

**Table 1.** Secondary organic aerosol potential (SOAP) in Warunawan Park, Kasetsart University

| Day | Isoprene | | α – piene | | β – piene | | Total SOAP |
|---|---|---|---|---|---|---|---|
| | VOCi | SOAP | VOCi | SOAP | VOCi | SOAP | |
| 19 April 2022 | 0.10±0.01 | 0.20 | 3.25±0.16 | 97.60 | 17.90±0.90 | 537.00 | 634.80 |
| 21 April 2022 | 0.37±0.02 | 0.74 | 1.13±0.05 | 33.90 | 2.73±0.14 | 81.90 | 116.54 |
| 26 April 2022 | 0.42±0.02 | 0.83 | 2.25±0.11 | 67.40 | 12.24±0.61 | 367.10 | 435.33 |
| 27 April 2022 | 2.40±0.12 | 4.81 | 3.27±0.16 | 98.10 | 42.14±2.11 | 1,264.20 | 1,367.11 |
| 03 May 2022 | 0.03±0.001 | 0.05 | 1.09±0.05 | 32.70 | 0.87±0.04 | 26.20 | 58.95 |
| 04 May 2022 | 1.57±0.08 | 3.15 | 1.10±0.06 | 32.90 | 2.82±0.14 | 84.50 | 120.55 |
| 10 May 2022 | 0.00 | 0.00 | 0.67±0.03 | 20.00 | 1.96±0.10 | 58.80 | 78.80 |
| Average | 0.70 | 1.40 | 1.82 | 54.66 | 11.52 | 345.67 | 401.73 |

Unit = $\mu g/m^3$

54.66, and, 345.67 $\mu g/m^3$, respectively. The highest total SOAP was 1,367.10 $\mu g/m^3$. This was primarily due to the dominance of the β-pinene concentration and β-pinene's FACi compared to isoprene and α-pinene. If β-pinene concentration varied, SOAP also changed. *Peltophorum pterocarpum*'s SOAP derived primarily from β – Pinene, α – piene and isoprene, respectively. SOA formation from monoterpenes and isoprene was dominated by •OH, which was confirmed by an increase in SOA yield and decrease in $NO_x$. The results demonstrated that the estimated SOA formation was related to temperature and light intensity, as shown in Figure 4. On April 27$^{th}$ 2022, the SOAP reached its highest level. On this day, the temperature and light intensity were notably the highest, at 35°C and 929.21 $\mu mol/m^2s$, compared to other days in the summer. These conditions likely induced heat stress in *Peltophorum pterocarpum*, causing the plants to produce and emit BVOCs as a stress-reduction mechanism. In urban areas, it was found that the concentrations of monoterpene and isoprene SOA tracers correlated with temperature [34].

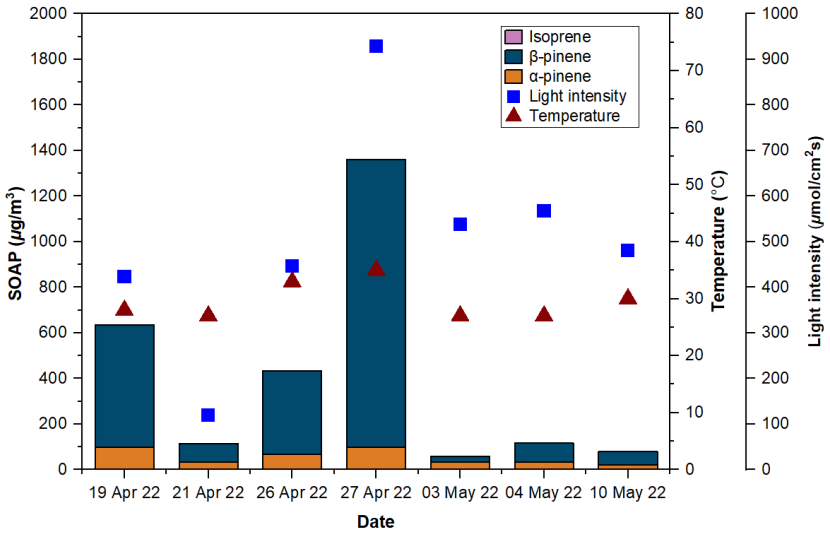


**Figure 4.** Total secondary organic aerosol potential (SOAP) and environmental conditions

### 3.2.2 Ozone formation potential (OFP)

The OFPs of isoprene, α – piene, and β – piene emission from *Peltophorum pterocarpum* are shown in Table 2. The average OFP of isoprene, α – piene, and β – piene were 7.41, 8.22, and, 40.56 $\mu g/m^3$, respectively. The OFPs varied with the BVOC concentration emitted by *Peltophorum pterocarpum*, temperature, and light intensity. On April 27$^{th}$, the highest OFP recorded was 188.58 $\mu g/m^3$, coinciding with the peak light intensity of 929.21 $\mu mol/m^2s$, as shown in Figure 5. Moreover, β-pinene and α-pinene have a higher potential to form $O_3$ than isoprene because they were high reactivity with ambient oxidants such as •OH and transform into $O_3$, according to Fu and Liao [35] and Berezina *et al.* [36]. In this study, $O_3$ could be formed by a photochemical reaction between BVOC, and oxidants under high NOx conditions by photochemical reaction in the daytime. BVOC reacted with •OH and generated Peroxy radicals (BVOC + •OH → $RO_2$•), and further reacted with NO and oxidized to $NO_2$ ($RO_2$• + NO → $NO_2$ + RO) which is then photolyzed by ultraviolet radiation ($NO_2$ + hv (<420 nm) → NO + O). These reactions led to the formation of ground-state oxygen atoms (O(3P)), which combine with oxygen ($O_2$) to produce $O_3$ ($O_2$ + O → $O_3$) [37], according to the Chapman reaction [38].

**Table 2.** Ozone formation potential (OFP) in Warunawan Park, Kasetsart University

| Day | Isoprene | | α – piene | | β – piene | | Total |
|---|---|---|---|---|---|---|---|
| | VOCi | OFP | VOCi | OFP | VOCi | OFP | OFP |
| 19 April 2022 | 0.10±0.01 | 1.06 | 3.25±0.16 | 14.67 | 17.90±0.90 | 63.01 | 78.74 |
| 21 April 2022 | 0.37±0.02 | 3.93 | 1.13±0.05 | 5.10 | 2.73±0.14 | 9.61 | 18.63 |
| 26 April 2022 | 0.42±0.02 | 4.42 | 2.25±0.11 | 10.13 | 12.24±0.61 | 43.07 | 57.63 |
| 27 April 2022 | 2.40±0.12 | 25.50 | 3.27±0.16 | 14.75 | 42.14±2.11 | 148.33 | 188.58 |
| 03 May 2022 | 0.03±0.001 | 0.28 | 1.09±0.05 | 4.92 | 0.87±0.04 | 3.07 | 8.27 |
| 04 May 2022 | 1.57±0.08 | 16.69 | 1.10±0.06 | 4.95 | 2.82±0.14 | 9.91 | 31.55 |
| 10 May 2022 | 0.00 | 0.00 | 0.67±0.03 | 3.01 | 1.96±0.10 | 6.90 | 9.91 |
| Average | 0.70 | 7.41 | 1.82 | 8.22 | 11.52 | 40.56 | 56.19 |

Unit = $\mu g/m^3$

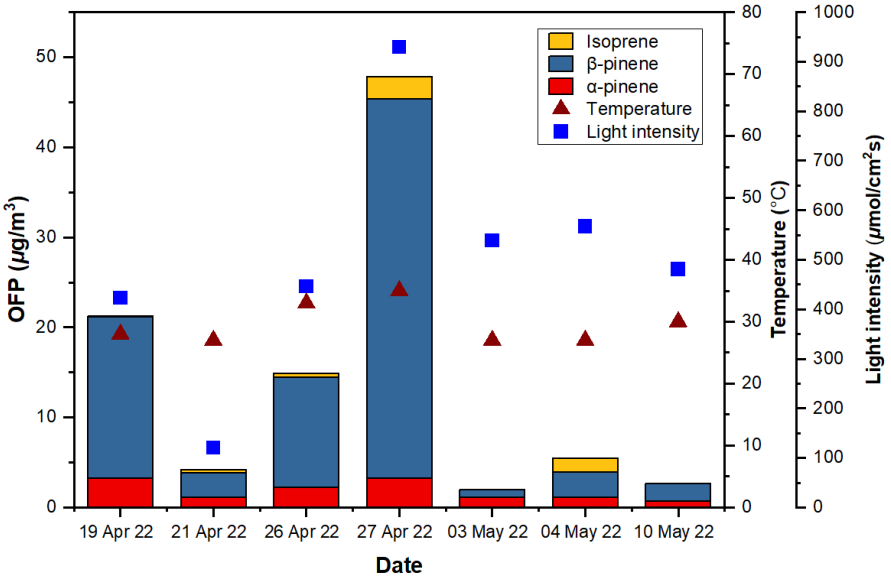


**Figure 5.** Ozone formation potential (OFP) in Warunawan Park, Kasetsart University

## 4. Conclusions

Urban air pollutants, especially SOAs and $O_3$, affect the environment and human health. The estimated potential secondary pollutant formation from BVOCs released from *Peltophorum pterocarpum* in urban areas, especially the formation of $O_3$ and SOA, can be determined using the maximum incremental reactivity (MIR) and fractional aerosol coefficient. The results demonstrated that the formation of $O_3$ and SOAs in the urban area was related to the BVOC concentration, temperature, and light intensity. The highest light intensity and temperature of 929.21 $\mu$mol/m$^2$s and 34.55 °C, respectively, resulted in BVOC emissions such as isoprene, α – piene, and β – piene at 2.40, 3.27 and, 42.14 $\mu$g/m$^3$, respectively, while $O_3$ was 188.58 $\mu$g/m$^3$ and SOA was 1,367.10 $\mu$g/m$^3$. The results showed that temperature and light intensity can affect BVOC emissions. However, the relationship of BVOC from plants and secondary pollutants in Thailand have not been widely investigated, and the role of secondary pollutants from BVOCs emitted by plants in urban areas should be considered in climate change adaptation plans.

## 5. Acknowledgements

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