Contribution of Terpenes to Ozone Formation and Secondary Organic Aerosols in a Subtropical Forest Impacted by Urban Pollution

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Abstract: The highly reactive nature of biogenic volatile organic compounds (BVOCs) impacts the biosphere by acting as a precursor of ozone and aerosols that influence air quality and climate. Here, we assess the influence of BVOCs and their oxidation products on ozone formation and to submicron secondary organic aerosol (SOA) mass in a subtropical forest. A high-resolution proton-transfer-reaction time-of-flight mass spectrometer (PTR-ToF-MS) was employed for the continuous measurement of VOCs. Isoprene, monoterpene, and sesquiterpene mixing ratios in the forest were 0.23, 0.22, and 0.03 ppb, respectively. The total ozone formation potential (OFP) of the terpenes was 12.8 µg m⁻³, which accounted for only 5.6% of the total OFP. Particle phase bound oxidation products were characterized using a thermal-desorption PTR-ToF-MS. Mass spectra analysis revealed the presence pinonaldehyde, pinonic, norpinonic, and pinic acid in both gas and particle phase. The overall daytime (nighttime) mixing ratio of the oxidized BVOCs in gas phases was 0.062(0.023) ppbv. On the other hand, the mean fraction of the four monoterpene oxidation products in condensed phase was estimated at 42%. Overall, the results of this study evidenced quantitatively the contribution of BVOCs to the total reactivity and SOA mass in the subtropical forest.

Keywords: BVOCs; TD-PTR-ToF-MS; ozone formation; SOA mass analysis

1. Introduction

Biogenic volatile organic compounds (BVOCs) produced by plants participate in large scale atmospheric processes that extend well beyond biogenic sites. Globally, the emission of BVOCs was calculated to be one order of magnitude higher from VOCs generated from human-related activities (e.g., automobile emissions and biomass burning). Every year, primary plant producers assimilate 1150 Tg of carbon, which is in turn released into the atmosphere as BVOCs [1]. Once emitted, BVOCs such as isoprene and monoterpene are oxidized through the reaction with hydroxyl radical
During daytime and with nitrate radical (NO$_3$) during nighttime. Oxidation of unsaturated BVOCs contributes to the total reactivity in a given area through the formation of ozone and OH radicals, as well as through the production of highly oxygenated compounds that impact secondary organic aerosol formation [2,3].

The overall emission of biogenic compounds is dominated by isoprene, a C$_5$ conjugated diene (C$_5$H$_8$, 2-methyl-1,3-butadiene). Top-down modeling indicated that the global emission of isoprene was at 500 Tg year$^{-1}$, which comprised almost half of the worldwide emission of BVOCs [4]. Modeling studies also showed that at a global level, the emission of isoprene is already comparable with the production of methane. The daytime concentration of isoprene follows the UV profile due to the absence of a buildup mechanism of isoprene in the leaves [5]. The highly reactive nature of isoprene limits the accumulation of isoprene in the atmosphere, which typically has a mixing ratio of less than 10 ppbv [6]. The dominant sink of isoprene is through the reaction with OH radical at $\tau_{OH}$~1.4 h and the subsequent formation of low volatility compounds from isoprene oxidation (e.g., dimers and organonitrates) significantly contributes to secondary organic aerosol (SOA) mass [7].

The emission of monoterpenes is crucial to the formation of secondary organic aerosol because of its high production rate from plants and the high yield for the SOA [8,9]. Monoterpenes are dimers of isoprene, with a general molecular formula of C$_{10}$H$_{16}$. The class of monoterpenes consists of thousands of compounds but only 20 compounds are usually detected at a significant amount in the atmosphere. Among them, $\alpha$-pinene is the largest contributor to the global emission of monoterpenes. Other monoterpenes include $\Delta$-carene, $\beta$-pinene, d-limonene, myrcene, etc. [10]. Oxidation of monoterpenes with OH and O$_3$ yields semivolatile organic compounds such as pinonaldehyde, pinonic acid, norpinonic, and pinic acid, which are suitable candidates for SOA formation [11].

Sesquiterpenes are less volatile terpenes, with a molecular formula of C$_{15}$H$_{24}$. Sesquiterpenes are easily oxidized compared to isoprene and monoterpenes, thus the sesquiterpenes are more efficient precursors for aerosol formation [12]. Due to the highly reactive nature of sesquiterpene and its high molecular weight, sesquiterpenes are limited within the tree canopy due to immediate oxidation with ozone [13]. Oxidation products of sesquiterpene include $\beta$-caryophyllene aldehyde, $\beta$-caryophyllonic acid, and 3,3-dimethyl2-(3-oxobutyl)-cyclobutanecarboxylic acid (DCCA). These compounds have low vapor pressure which makes these compounds essential in aerosol formation [14]. Overall, the major BVOCs isoprene, monoterpenes, sesquiterpene, play a crucial role in the formation of SOA generated in biogenic environments, which later participate in important atmospheric processes such as the formation of cloud condensation nuclei. Moreover, global BVOC emissions are much higher compared to anthropogenic VOC emissions, thus understanding the behavior of these BVOCs and their oxidation products will provide valuable insights on air quality climate on a regional and global scale.

Due to wide-scale development, urban environments are getting closer to biogenic environments and the response of natural systems to human-related emissions is still not fully comprehended. For instance, the enhancement of sulfur dioxide (SO$_2$) from anthropogenic emissions in forest leads to the formation of sulfuric acid via the interaction of SO$_2$ with water. This in turn causes acid precipitation that directly damages the trees [15]. Moreover, in the absence of urban air pollution, terpenes and NO$_x$ from natural sources effectively eliminates toxic atmospheric pollutants. Excess NO$_x$ transported from urban environments leads to deviation to natural balance and enhancement of production of secondary photochemical pollutants [16]. In the Amazon rainforest, emission of NO$_x$ from a nearby metropolis city (Manaus) elevated the production of biogenic SOA by 60%–200% [17]. Besides, the transport of NO$_x$ to forest modifies the atmospheric distribution of oxygenated products from the oxidation of the terpenes. This leads to the evident formation of organonitrates instead of first-generation compounds such as pinonic acid, pinonaldehyde, and later highly oxygenated molecules (HOMs), which in turn can suppress particle formation and lower SOA mass yield. Indeed, the transport of anthropogenic compounds to the forest sites can alter the impact of BVOCs in relevant atmospheric processes such as SOA production and ozone formation [18,19].
Here, we present the measurement of the BVOCs and their oxidation products both in gas and particle phase in a subtropical forest during a 30-day sampling campaign in East Asia using a modified PTR-ToF-MS [20]. The contribution of the BVOCs to ozone formation and SOA mass is assessed to determine the overall atmospheric participation of BVOCs in a biogenic site impacted by urban pollution transported from a nearby metropolis area.

2. Experiments

2.1. Site Description and Instrumentation

The measurements were carried out at the Xitou Experimental Forest of National Taiwan University, located in Nantou, Taiwan (23°92' N, 120°77' E), from 6 October to 5 November 2015. The Xitou forest is 1120 m above sea level with an area of 2500 hectares, primarily composed of cypresses and ginkgo trees. The forest is situated in a concave valley and surrounded by three different mountains. The temperature and relative humidity in the experimental forest averaged at 20.5 °C and 91%. The daytime submicron particulate matter (PM$_{1.0}$) and carbon monoxide (CO) were 28 ± 11 µg m$^{-3}$ and 250 ± 43 ppb, respectively. Daytime sulfur dioxide (SO$_2$) and nitrogen dioxide (NO$_x$) had a mean concentration of 0.21 ± 0.13 ppb and 2.3 ± 0.6 ppb, respectively. The elevated concentration of such anthropogenic pollutants indicates the evident transport of the urban pollutants to the biogenic site. In addition, a previous study reported substantial transport of urban-related pollutants to Xitou forest through mountain-valley circulation and long-range transport from regional sources. Ozone and PM were transported from downhill areas where municipal waste incinerators, coal combustion power plants, and industrial sources are present. [21]. This forest site is described in detail in previous publications [20,21].

The instruments used in this study were housed in a wooden cabin with proper ventilation. Several online instruments were co-located during the field study to monitor the concentration of analytes in the gas and condensed phase. The VOCs were measured using a proton-transfer-reaction time-of-flight mass spectrometer (PTR-ToF-MS 8000, IONICON Analytik, Innsbruck, Austria) at 132 E/N ratio (Townsend). Description of the general technique of the PTR-ToF-MS can be found elsewhere [22]. Briefly, VOCs (M) are protonated via non-dissociative proton transfer using hydronium ions ($H_3O^+$) in the drift tube, as shown in Equation (1):

$$H_3O^+ + M \rightarrow H_2O + MH^+ \tag{1}$$

PTR-ToF-MS detects compounds such as carboxylic acids, carbonyls, and aromatic hydrocarbons with proton affinity higher than water (691 kJ/mol). The PTR-ToF-MS was calibrated daily using a 110-ppb mixture of gases (isoprene, limonene, benzene, toluene, ethylbenzene, dichlorobenzene, trichlorobenzene, and trimethylbenzene, Restek Corp). An advanced Liquid Calibration Unit (LCU-a, IONICON Analytik, Innsbruck, Austria) was utilized to dilute the gaseous standard (110 ppb) for calibration range of 1.0 to 20 ppb with high precision. The absolute mixing ratios of isoprene, monoterpene, and sesquiterpene (expressed as ppbv) were determined using PTR-ToF-MS via first-order kinetic reaction, which is expressed by the equation below:

$$[RH^+] = [H_3O^+]_0 (1 - \exp(-k[R] \Delta t)) \tag{2}$$

where $k$ is the reaction rate constant, $[H_3O^+]_0$ is the signal of the reagent ions before the proton transfer, $[R]$ is the overall concentration of the VOC in the drift tube and $\Delta t$ is the reaction time for the reagent ion in the drift tube. This is complemented by transmission efficiency analysis using standard VOCs with different molecular weights [23] Ozone was measured using a UV photometry instrument (Thermo Scientific Model 49i, Waltham, MA, USA). Nitrogen oxides (NO and NO$_2$) were measured using a tandem of chemiluminescence analyzer (CLD 88 p, ECO PHYSICS, Duernten, Switzerland) and photolytic converter (PLC 860, ECO PHYSICS Duernten, Switzerland). Moreover, PM1 was
collected using a pair of US federal reference method samplers (PQ-200, BGI Inc.) equipped with sharp cut cyclones. The PM1 samplers were loaded and replaced twice daily with a Teflon filter and a double-layered quartz filter (QBQ set-up), respectively. The sampling duration of the PM1 samplers was from 9:00 to 18:00 (“daytime”) and from 20:00 to 06:00 (“nighttime”), local time. Most of the data presented in this study used the daytime samples unless indicated otherwise.

2.2. Characterization of the Particle-Bound Organic Compounds Using TD-PTR-ToF-MS

A modified thermal desorption unit (DRI Model 2001A, Atmoslytic, Inc., Calabasas, CA, USA) was utilized to evaporate the organic compounds from a 0.528 cm$^2$ punch quartz filter. The desorption unit was designed to desorb the organic compounds in a stepwise manner with a five-minute interval each step. The four target temperatures were 100 °C, 200 °C, 350 °C, and 550 °C. Ultra-pure nitrogen (99.9995%, Air Products) was used as the carrier gas and a heated transfer line (95–100 °C) served as the connector between the desorption unit and the PTR-ToF-MS. At the same time, the inlet temperature of the PTR-ToF-MS was set at 100 °C, to minimize condensation loss. A detailed description of the whole TD-PTR-ToF-MS tandem unit can be found in prior studies [20,24].

The mass concentration of the identified ions from the thermal desorption was calculated using the following equation:

$$n_{\text{aer},M} = \frac{C_{\text{ave},M} \times MW_M \times F_{N2} \times t_{\text{meas}}}{22.4 \times F_{\text{col}} \times t_{\text{col}} \times 0.001 \times F_{\text{filter}}}$$

(3)

where $n_{\text{aer},M}$ is the mass concentration of an organic compound (M) in ng m$^{-3}$, $C_{\text{ave},M}$ is the average of the mixing ratio (ppb) measured by the PTR-ToF-MS at a given time of measurement ($t_{\text{meas}}$), and flow rate of the carrier gas ($F_{N2}$), which were 20 min and 0.095 LPM, respectively. The $F_{\text{col}}$ and $t_{\text{col}}$ are the flow rate and sampling time duration of the aerosol sampler (PQ-200), which were 16.7 LPM and 9 h for daytime and 10 h for nighttime. $F_{\text{filter}}$ is the fraction of the quartz filter introduced to the TD-PTR-ToF-MS unit using a customized platinum boat.

2.3. Mass Concentration and Organic Carbon Analysis

Filters were immediately stored in a refrigerator (~8 °C) after the aerosol collection and shipped back every week to the laboratory for chemical analysis. Gravimetric analyses of the Teflon filters were done using a microbalance (Model XP6, Mettler Toledo Columbus, OH, USA). Organic Carbon/Elemental Carbon (OC/EC) analysis of quartz filters was done using DRI Model2001A Thermal/Optical Carbon Analyzer (Atmoslytic, Calabasas, CA, USA) with IMPROVE_A method. Particulate organic matter (OM) from OC data was determined using 1.6 as a conversion factor [25]. The value of 1.6 was assigned for urban aerosols while non-urban areas such as Xitou forest site should utilize 2.1. However, we believe that the forest site was heavily impacted by urban processes, thus utilizing the 1.6 factor appears to be reasonable for this case.

3. Results and Discussion

3.1. Terpene Mixing Ratios and Contribution to Ozone Formation

The behavior of isoprene, monoterpenes, and sesquiterpenes, which mostly comprise the global BVOC budget, is addressed in this section. Figure 1 shows the mixing ratio of the major terpenes in the Xitou forest. The overall mixing ratios of isoprene, monoterpenes, and sesquiterpenes were 0.23 ± 0.22, 0.22 ± 0.12, and 0.03 ± 0.02 ppb. The sub-ppbv mixing ratio of isoprene was lower compared to other forest systems with typical concentration above 1 ppb [26,27]. The mixing ratios of isoprene and monoterpenes are comparable, unlike in other biogenic sites where isoprene typically dominates the atmospheric BVOC budget. This reflects the mixed flora system planted in the experimental forest in Central Taiwan. Isoprene concentration in the Xitou forest is comparable in Landes Forest in France [28] but significantly lower compared to measurements done in a temperate forest in the United States [29] and in a rain forest in Central Amazon [30]. The lower concentration of isoprene can be accounted to
the higher reactivity in Xitou forest, which consumed the freshly emitted isoprene before reaching the measurement cabin. Moreover, monoterpene concentration in the Xitou forest was evidently lower compared to tropical forest (~3.0 ppb) [31] and to temperate forests (~6.0 ppb) [28] but comparable to mixing ratios reported in a boreal forest (~0.25 ppbv) [32]. Online measurements of sesquiterpene are typically underestimated due to extensive fragmentation. Nonetheless, sesquiterpene recorded in Xitou forest was elevated compared to a boreal site [33] and tropical forest [13].

**Figure 1.** Time series and average diurnal (inset) profile of isoprene, monoterpene, and sesquiterpene.

The daytime (nighttime) mean concentration of isoprene, monoterpene and sesquiterpene were $0.44 \pm 0.20$ ($0.07 \pm 0.02$), $0.18 \pm 0.07$ ($0.25 \pm 0.10$), and $0.02 \pm 0.01$ ($0.03 \pm 0.01$) ppb, respectively. The daily max concentration of isoprene occurred between 10:00 and 17:00, while the strong enhancement of monoterpene (sesquiterpene) was observed at 18:00 (8:00). The diurnal profile of isoprene followed the UV and temperature profile, consistent with the induced production of isoprene with sunlight. On the other hand, biogenic emission of monoterpene and sesquiterpene were favored during nighttime, indicating that the emissions of larger terpenes were not temperature and light-dependent in the Xitou forest. Lower concentration of mono- and sesquiterpene were accounted by the rapid oxidation with OH radicals, which in turn produce multi-generation biogenic products that persist both in gas and condensed phase.

With elevated NO$_x$ concentration during daytime (up to ~5 ppb, see Figure S4 in Supplementary Materials), ozone formation from VOC in the forest impacted by urban pollution is evident. The chemical reactivity and impact of terpenes to ozone formation can be quantified using incremental reactivity, given by the response of the ozone concentration to an incremental increase of VOC, divided by
the total mixing ratio of VOC. In particular, the ozone formation potential (OFP) \cite{34,35} of isoprene, monoterpene, and other VOCs in the subtropical forest were determined as the product of the mixing ratio of VOCs ([VOC]) and the maximum incremental reactivity coefficient (MIR), given by the equation:

\[
OFP_i = [\text{VOC}]_i \times \text{MIR}_i
\]  

(4)

To minimize the computational cost, only the top 25 compounds in terms of VOC reactivity and mixing ratio were considered. The OFP calculated in this study should be treated as a lower limit due to the limited capacity of the PTR-ToF-MS to measure reactive compounds such as methane, ethane, propane, butane, ethene, and acetylene with proton affinity lower than that of water. Table 1 lists the calculated ozone formation potential of the dominant VOCs in the forest. These major compounds attributed 230 $\mu$g m$^{-3}$ OFP. Isoprene, monoterpene, and sesquiterpene contributed 6.9, 5.6, and 1.7 $\mu$g m$^{-3}$, accounting for 3.0, 2.4, and 0.3% of the total OFP. Overall, the major BVOCs only contributed 5.7% of the total OFP. During the highest emission of isoprene at midday, the reactivity of isoprene to form ozone was only at 15 $\mu$g m$^{-3}$. These were significantly lower compared to measurements in different sites in China \cite{36} and Iberian Peninsula \cite{37}, due to low biogenic activity in the forest and the contribution of other major compounds to the formation of ozone. Highly reactive compounds such as propene, butene, acetaldehyde, and formaldehyde, which have primarily anthropogenic origins, accounted 44.0, 37.0, 18.9, and 17.8 $\mu$g m$^{-3}$ to the formation of ozone, with an overall 50% contribution to total reactivity in the forest. Clearly, anthropogenic compounds transported from urban environments dominated the overall reactivity in the biogenic site.

**Table 1.** The concentration of the most abundant volatile organic compounds (VOC) species and their ozone forming potential (OFP) in Xitou forest. Compounds inside the parenthesis are the basis for the maximum incremental reactivity coefficient (MIR) for compounds with multiple isotopes. Source A: anthropogenic; B: biogenic.

| Compound                  | Molecular Weight | Mixing Ratio (ppbv) | Source | OFP (µg m$^{-3}$) | %Cont. to Total OFP |
|---------------------------|------------------|---------------------|--------|-------------------|---------------------|
| Propene (1-propene)       | 42.08            | 2.16                | A/B    | 49.31             | 19.13               |
| Butene (1-butene)         | 56.11            | 1.63                | A/B    | 36.92             | 16.08               |
| Acetaldehyde              | 44.05            | 1.58                | A/B    | 18.87             | 8.22                |
| Formaldehyde              | 30.03            | 1.52                | A/B    | 17.87             | 7.78                |
| Ethanol                   | 46.07            | 5.47                | A/B    | 15.99             | 6.97                |
| Acrylic acid              | 72.06            | 0.41                | A/B    | 13.86             | 6.04                |
| Methacrylic acid          | 86.09            | 0.19                | A      | 12.42             | 5.41                |
| Butanal                   | 72.11            | 0.52                | A/B    | 9.33              | 4.06                |
| Methyl Vinyl Ketone       | 70.09            | 0.29                | B      | 8.21              | 3.57                |
| Pentanal                  | 84.12            | 0.43                | A/B    | 7.55              | 3.29                |
| Isoprene                  | 68.12            | 0.23                | B      | 6.9               | 3                   |
| Hexanal                   | 100.16           | 0.34                | A/B    | 6.07              | 2.64                |
| Pentene (1-pentene)       | 70.14            | 0.28                | A/B    | 5.97              | 2.6                 |
| Monoterpene (a-pinene)    | 136.23           | 0.22                | B      | 5.61              | 2.44                |
| Toluene                   | 92.14            | 0.28                | A      | 4.25              | 1.85                |
| Ethylbenzene              | 106.17           | 0.1                 | A      | 2.87              | 1.25                |
| Methanol                  | 32.04            | 2.87                | A/B    | 2.56              | 1.11                |
| 1,2,3-trimethyl benzene   | 120.19           | 0.04                | A      | 2.27              | 0.99                |
| Hexene (1-hexene)         | 84.16            | 0.11                | A/B    | 2.18              | 0.95                |
| m-diethyl benzene         | 134.22           | 0.05                | A      | 1.94              | 0.85                |
| Acetic acid               | 60.05            | 1.0                 | A/B    | 1.7               | 0.74                |
| Acetone                   | 58.08            | 0.97                | A/B    | 0.84              | 0.37                |
| Sesquiterpene (C15 alkene)| 204.35           | 0.02                | B      | 1.71              | 0.29                |
| Propionic acid            | 74.08            | 0.17                | A/B    | 0.62              | 0.27                |
| Benzene                   | 78.11            | 0.23                | A      | 0.53              | 0.23                |
| Formic acid               | 46.03            | 3.2                 | A/B    | 0.4               | 0.18                |
3.2. Oxidation Products of Monoterpenes in Gas and Particle-Phase

Four oxygenated hydrocarbons (C\textsubscript{x}H\textsubscript{y}O\textsubscript{z}) from the oxidation of monoterpenes were detected both in the gas and condensed phases. Nitrogen containing compounds (C\textsubscript{x}H\textsubscript{y}O\textsubscript{z}N\textsubscript{w}) produced from monoterpene and isoprene were discussed in a separate study [20]. These four oxygenated hydrocarbons were not previously reported in an urban site (Metropolitan Taipei), which used the same analytical procedure with this study [24]. Moreover, a strong association among the time series of the biogenic products in both gas and particle phase was observed, clearly indicating that these BVOCs had a strong single biogenic source (see Figure S1 in Supplementary Materials). One of the major differences between the major peaks observed in the urban (Taipei) and the sub-tropical forest site was the evident emergence of the peak at \textit{m/z} 71. This fragment was accounted to the most abundant fragment of cis-pinonic acid (C\textsubscript{10}H\textsubscript{16}O\textsubscript{3}) [24]. Pinonic acid is a first-generation product of oxidation of pinene [9,38]. The other three potential biogenic markers are the peaks at 151, 153, and 167 \textit{m/z} which were assigned as fragments of pinonaldehyde, norpinonic acid, and pinic acid. The peaks at 153 and 167 \textit{m/z} are the acylium fragments (RCO\textsuperscript{+}) of the two acids, while the peak at 151 was a result of dehydration of pinonaldehyde and its keto-enol tautomerization and rearrangement. These biogenic tracers are oxidation products of both ozone and OH radical initiated reactions of \(\alpha/\beta\)-pinene. Figure 2 shows the near explicit production pathway of the four biogenic markers, from the oxidation of \(\alpha/\beta\)-pinene and their subsequent partitioning to the condensed phase (red lines).

![Figure 2](image-url)
3.2.1. Gas Phase

Figure 3 shows the daily profile of the three monoterpane oxidation products in gas phase. Pinonic acid, measured at m/z 71 fragment, was not included here due to interference from methyl vinyl ketone and methyl acrolein (C₄H₆O), which are first-generation oxidation products of isoprene, at the same exact mass (71.049 m/z). The daytime (nighttime) mixing ratio of pinonaldehyde, norpinonic, and pinic acid were 0.019 ± 0.017 (0.006 ± 0.020), 0.023 ± 0.015 (0.008 ± 0.020) and 0.021 ± 0.021 (0.007 ± 0.020) ppbv. The dominant persistence of the BVOCs during daytime suggests that their primary production pathway is through photochemistry. Furthermore, a consistent pattern was observed for the BVOC oxidation products, with a strong peak at 13:00 and minor shoulder at 8:00. The enhancement of mixing ratio at 13:00 is consistent with the peak of the UV (sunlight) radiation which induced the OH radical initiated formation of the BVOCs. The minor peak at 8:00 was accounted to the formation burst of the oxygenated BVOCs due to the initial exposure of UV at sunrise to the accumulated monoterpane in the atmosphere throughout the night. This highlights the contribution of precursor VOCs, where the evident availability of the monoterpenes translates to more oxidation products. Other than UV, temperature also induced the formation of BVOCs, based on the association of the mixing ratio of the BVOCs with temperature (see Figure S2 in Supplementary Materials). Higher temperature conditions increased the rate of transformation of monoterpane to pinonaldehyde, norpinonic, and pinic. Average concentrations of the biogenic organic species both in gas and condensed phase are given in the Supplementary Materials (Table S1).

![Figure 3](image.png)

**Figure 3.** Diurnal profile of (a) pinonaldehyde, (b) norpinonic, and (c) pinic acid in gas phase measured in the subtropical forest. The shaded area is the variability of measurement given by 1 standard deviation. Time series profiles are given in the Supplement.

3.2.2. Particle Phase

The average daytime mass concentration of submicron particles in the Xitou forest was 21 µg m⁻³, with 36% attributed to the organic matter portion. Among the biogenic tracers, pinonic acid was the most dominant species contributing to OM. Pinonic acid contributed 0.88% to OM mass, with an average mass concentration of 65 ± 36 ng m⁻³ (max: 170 ng m⁻³). Mass concentration of pinonic acid in other forest and urban sites were typically below 50 ng m⁻³ [39–42] and the high concentration of pinonic acid in the Xitou forest was attributed to the high daytime ozone mixing ratio (O₃ave = 53 ppb) and the elevated relative humidity. Weak dependence of particle bound pinonic acid with temperature (r = 0.09) was observed in the forest. The partitioning of the gas phase compounds to the condensed phase is temperature-dependent, thus the observed mass concentration of pinonic acid should show strong reliance with the ambient temperature. Daytime temperature (Tave = 20 °C) in the forest was relatively stable, with day-to-day variability of almost 1 °C, which explains the weak of the association between temperature and the mass concentration of pinonic acid in the particle phase. For the other oxygenated BVOCs, better relationship with temperature was observed but still considered as weak (see Figure S2 in Supplementary Materials). Like pinonic acid, mixing ratios of pinonaldehyde (40 ng m⁻³) and pinic
Acid (50 ng m\(^{-3}\)) were enhanced compared to previous observations \[40,42\], which was credited to the elevated R.H. in the forest. During the field measurement, the mean RH was 95%, which induced the partitioning of the oxidized species to the particle phase. Previously, the mean fraction (\(F_{\text{part}}\)) of pinonaldehyde in the condensed phase has been shown to increase with R.H. \[43\]. For this case, \(F_{\text{part}}\) is given by the equation:

\[
F_{\text{part}} = \frac{[\text{BVOC}]_{\text{part}}}{[\text{BVOC}]_{\text{part}} + [\text{BVOC}]_{\text{gas}}} \tag{5}
\]

Here, \([\text{BVOC}]_{\text{part}}\) and \([\text{BVOC}]_{\text{gas}}\) are the concentration of the oxygenated BVOC in particle and gas phase, respectively. The mean fraction of pinic acid, norpinic acid, and pinonaldehyde in the particle phase was 42%. A moderate dependence of the \(f_{\text{part}}\) of the BVOCs with R.H. was observed for pinic acid, showing the effect of atmospheric water content in the partitioning of oxygenated BVOCs in the condensed phase (see Figure S3 in Supplementary Materials). Even with the enhancement due to elevated atmospheric water content, the four major oxidation products of monoterpene in the condensed phase only contributed 3% of OM. The other portion of OM was attributed to the partitioning of anthropogenic compounds such as phthalic acid and levoglucosan, which have urban and biomass burning sources. These anthropogenic compounds in the condensed phase will be further explained in a succeeding study, which will provide an in-depth analysis of their formation and partitioning to biogenic SOA. As a reference, the top five most abundant compounds alone, which all had anthropogenic origin, contributed as much as 20% of the total OM.

### 3.2.3. Influence of Precursor and Oxidants on Oxygenated BVOCs

Both the OH and O\(_3\) initiated oxidation reactions of \(\alpha/\beta\)-pinene yield the four biogenic compounds (as shown in Figure 2) but at varying rates. Several routes of formation of these markers make it difficult to associate a dominant factor such as precursor VOC, atmospheric components (e.g., oxidants and NO\(_x\)), and metrology that directly affect the concentration of these compounds in the condensed phase. To simplify the analysis, the four biogenic markers in the particle phase were clumped as a single monoterpene oxidation product to further understand the overall factor/s contributing to the production of biogenic compounds in the forest. The average mass concentrations of each biogenic marker were relatively comparable; thus, no single organic compound will dominate the overall feature of the clumped tracer. Figure 4 shows the daytime time series of the clumped biogenic tracer, together with ozone and monoterpene. As a reference, the average concentrations of the biogenic tracers, monoterpene, and ozone for the whole campaign period were 249 ng m\(^{-3}\), 0.24 ppb, and 54 ppb. Two prominent time regions highlighted the influence of precursor and oxidants. The latter portion of the field measurement (30 October–5 November) showed a low mass concentration of biogenic tracers (202 ng m\(^{-3}\)), which was attributed to low biogenic activity in the forest leading to the weak emission of monoterpene (0.13 ppb). On the other hand, evident enhancement (p-value = 0.001) of biogenic tracers was evident between 13 October to 19, with a mass concentration of the oxygenated BVOCs 30% higher (281 ng m\(^{-3}\)) compared to the campaign average. The mixing ratio of monoterpene (0.27 ppb) during this period was comparable with the campaign average, thus the behavior of the monoterpene was not the dominant factor for the formation of the biogenic tracers during this time. Instead, elevated oxidation processes, signified by the high mixing ratio of ozone (70 ppb), induced the formation of these biogenic markers. Overall, this shows that the local levels precursor VOC and oxidants in the forest appreciably influenced the formation and partitioning of biogenic oxidation products to particle phase, with minor contributions from ambient metrological conditions.
Figure 4. Time series profile of the mass concentration of clumped biogenic tracers including pinonic, pinic, norpinonic acid, and pinonaldehyde. Moreover, included in the figure are the time series of ozone and sum of monoterpene mixing ratios.

4. Summary and Conclusions

Gas and particle-phase measurements of biogenic organic compounds were conducted in Xitou forest in Central Taiwan using a PTR-ToF-MS from October to November 2015. The daytime (nighttime) average mixing ratio of isoprene, monoterpene and sesquiterpene were $0.44 \pm 0.20$ ($0.07 \pm 0.02$), $0.18 \pm 0.07$ ($0.25 \pm 0.10$), and $0.02 \pm 0.01$ ($0.03 \pm 0.01$) ppbv, respectively. Isoprene followed the UV profile with a daytime peak, while monoterpene and sesquiterpene showed nighttime accumulation. Generally, the terpene concentration observed in the Xitou forest was low, which was attributed to low biogenic activity during the fall–winter season and the possible rapid oxidation of terpenes occurred in the subtropical forest. Furthermore, terpenes contributed $13.8 \mu g m^{-3}$ to the ozone formation potential, accounting $5.7\%$ of the total reactivity in the forest. In comparison, the OFP of formaldehyde, acetaldehyde, butene, and propene, which have both biogenic and anthropogenic sources, accounted $50\%$ of the total OFP. The possible transport of anthropogenic gas-phase pollutants to the subtropical forest could have overshadowed the contribution of terpenes to the total reactivity in the biogenic site.

Four oxidation products of monoterpene (pinonaldehyde, pinonic, norpinonic, and pinic acid) were detected both in gas and condensed phase. The daytime (nighttime) mixing ratio of pinonaldehyde, norpinonic, and pinic acid were $0.019 \pm 0.017$ ($0.006 \pm 0.020$), $0.023 \pm 0.015$ ($0.008 \pm 0.020$) and $0.021 \pm 0.021$ ($0.007 \pm 0.020$) ppbv. The enhanced mixing ratio of the first-generation oxidation products of monoterpene during daytime indicates that photochemistry is the favored production pathway of the oxygenated BVOCs in the subtropical forest. A minor peak was observed on sunrise due to the initial exposure of the accumulated monoterpene to UV radiation (~8:00 AM) which lead to the formation burst of the oxygenated BVOCs. The mass concentration of the oxidation products in the condensed phase was elevated compared to previous measurements of the same BVOCs, which was due to the higher water content of the atmosphere ($R.H_{ave} > 90\%$). This preferred the partitioning of the oxygenated BVOCs to the condensed phase, with $42\%$ of the produced BVOC partitioned to the particle phase. Moreover, during certain periods in the measurement, the mixing ratio of monoterpene and oxidants impacted the production and the subsequent partitioning of the oxygenated BVOCs to the condensed phase. It was also noticed that the oxidation products of monoterpene, including the organonitrates detected in a previous study [20], altogether attributed only $5\%$ of OM in the forest even
though these four compounds are the major product of C_{10} terpenes. Contribution from anthropogenic (e.g., urban and biomass burning activities) sources was suspected to dominate the formation of SOA in the subtropical forest. A prior study indicated a massive transport of anthropogenic emissions to Xitou forest from an urban metropolis region (Taichung) and its nearby areas, as well as through long-range transport from regional sources [21]. This augmented the mass concentration of SOA through the partitioning of urban and biomass burning related compounds such as dicarboxylic acids (e.g., phthalic and succinic acid) and levoglucosan. This warrants the further characterization of other tracers, particularly the anthropogenic markers, in the condensed phase to fully comprehend the dynamic air quality in the subtropical forest.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4433/11/11/1232/s1, Figure S1: Correlation analysis map of atmospheric concentration of the oxidation products of monoterpene in gas and condensed phase, Figure S2: Effect of temperature on the production of BVOC in the gas and particle phase, Figure S3: Correlation of mean fraction of BVOC in the particle phase with atmospheric water content, Figure S4: Time series mixing ratio of NOx in Xitou forest, Figure S5: Time series profile of pinonaldehyde, norpinonic, and pinic acid in gas phase, Table S1: Average mixing ratio (ppbv) of the BVOCs in gas phase, Table S2: Mass concentration (ng m^{-3}) of monoterpene oxidation species in the particle phase measured in Xitou forest.

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