Research article

Modeling the effect of VOCs from biomass burning emissions on ozone pollution in upper Southeast Asia

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ABSTRACT

We used a Weather Research and Forecasting Model with Chemistry (WRF-CHEM) model that includes anthropogenic emissions from EDGAR-HTAP, biomass burning from FINN, and biogenic emissions from MEGAN to investigate the main volatile organic compound (VOC) ozone precursors during high levels of biomass burning emissions in March 2014 over upper Southeast Asia. A comparison between the model and ground-based measurement data shows that the WRF-CHEM model simulates the precipitation and 2 m temperature reasonably well, with index of agreement (IOA) values ranging from 0.76 to 0.78. Further, the model predicts O3, NO2, and CO fairly well, with IOA values ranging from 0.50 to 0.57. However, the magnitude of the simulated NO2 concentration was generally underestimated compared to OMI satellite observations. The model result shows that CO and VOCs such as BIGENE play an important role in atmospheric oxidation to surface O3. In addition, biomass burning emissions are responsible for increasing surface O3 by ~1 ppmv and increasing the reaction rate of CO and BIGENE by approximately 0.5 × 106 and 1 × 106 molecules/cm2/s, respectively, in upper Southeast Asia.

1. Introduction

O3 is a major air pollutant that can have negative effects on human health, agriculture, weather, and climate (Nuvolone et al., 2018; Felzer et al., 2007; Ebi and McGregor, 2008). For example, Bell et al. (2004) and Bell and Dominici (2008), who investigated the health effects of O3 exposure in the United States in 1987–2000, found that a 10 ppbv increase in ozone was associated with a 0.52% increase in mortality and a 0.64% increase in cardiovascular and respiratory mortality. Recent calculations of global premature mortality rates based on high-resolution global model simulations of O3 and PM2.5 revealed that Southeast Asia and the Western Pacific have the highest premature mortality rates worldwide, which account for approximately 25% and 45% of the global mortality rate in 2005, respectively (Lelieveld et al., 2013). The total number of regional premature deaths from anthropogenic ozone is estimated to be approximately 33,300 in Southeast Asia (Lelieveld et al., 2013). The effect of O3 on the agricultural ecosystem was reviewed by Lenka and Lenka (2012), who presented evidence of a reduction in crop yields due to increasing levels of O3 and suggested that this effect may partially explain the decline in crop yields in South Asia. As reported by Amnuaylojaroen et al. (2018), with changes in the climate and emissions, the O3 levels over Southeast Asia will tend to increase by 10%–27% in the future. In addition, O3 also plays a central role in tropospheric chemistry as a precursor of the hydroxyl (OH) radical, which acts as a detergent in the atmosphere. Therefore, it is very important to understand the processes controlling the formation and distribution of O3.

O3 is not directly emitted by anthropogenic or natural sources, but instead is the product of photochemistry between volatile organic compounds (VOCs), nitrogen oxides (NOx = NO + NO2), and carbon monoxide (CO). Though often present at levels of only 1 ppb or less, nitrogen oxides play a central role in the chemistry of the troposphere (Melkonyan and Kuttler, 2012). The gas-phase chemistry of the troposphere involves the oxidation of organic molecules in the presence of nitrogen oxides under the influence of sunlight. Atmospheric oxidation proceeds via chains of free radical reactions. Because atmospheric oxidation involves a very dilute fuel, at mixing ratios of parts per million or even parts per billion, an external source of energy is required to drive the reactions, and that energy is provided by solar radiation (Seinfeld and Pandis, 1998). In the urban and continental troposphere, many other anthropogenic and biogenic hydrocarbons and organic species are present. As a result of combustion emissions, greatly enhanced levels of NOx over those in the background troposphere exist in urban and continental areas.
and NO\textsubscript{2} is the key constituent affecting the chemistry of the troposphere (Hagenbirk et al., 2017). O\textsubscript{3} is considered to be the principal product of tropospheric chemistry. NO\textsubscript{2} plays an important role in ozone formation. Specifically, ozone forms as a product of NO\textsubscript{2} photolysis. Then, it is destroyed rapidly in the presence of NO (Seinfeld and Pandis, 1998), as follows:

\[
\text{NO}_2 + h\nu + O_2 \rightarrow NO + O_3
\]

\[
O + O_3 \rightarrow O_2
\]

\[
O_3 + NO \rightarrow NO_2 + O_2
\]

Further, carbon monoxide reacts with the hydroxyl radical, and the hydrogen atom combines very quickly with O\textsubscript{2} to form the hydroperoxy radical HO\textsubscript{2}. When NO is present, the most important atmospheric reaction that HO\textsubscript{2} undergoes is that with NO. Net formation of O\textsubscript{3} occurs in the reaction because NO is converted to NO\textsubscript{2} by the HO\textsubscript{2} radical rather than by O\textsubscript{3} itself (Seinfeld and Pandis, 1998).

The atmospheric oxidation of CO can be summarized as follows:

\[
O + OH \rightarrow CO_2 + H
\]

\[
H + O_3 \rightarrow HO_2
\]

\[
CO + OH \rightarrow CO_2 + HO\textsubscript{2}
\]

\[
\text{HO}_2 + NO \rightarrow NO_2 + OH
\]

\[
\text{NO}_2 + h\nu \rightarrow NO + O
\]

\[
O + O_3 \rightarrow O_2
\]

In areas of high population, ozone formation can be enhanced by VOC emissions (European Environment Agency, 2008). The photochemical reaction that produces ozone is initiated and maintained by reactive radicals. In the process, other products are formed, such as peroxacyetyl nitrate (PAN), nitric acid, aldehydes, organic acids, particulates, and many short-lived radical species. VOCs act as “fuel” in the ozone formation process, whereas NO functions more or less as a catalyst, because it is regenerated in the formation process. NO also plays a key role in the regeneration of the reactive radicals and the further progress of the reactions. The simplified photochemistry of ozone, which in reality is a complex and highly nonlinear process (European Environment Agency, 2008) is shown below:

\[
\text{VOC} + OH + O_2 \rightarrow \text{RO}_2 + H_2O
\]

\[
\text{RO}_2 + NO + O_3 \rightarrow NO_2 + HO_2
\]

\[
\text{HO}_2 + NO \rightarrow NO_2 + OH
\]

\[
\text{NO}_2 + h\nu + O_3 \rightarrow NO + O_3
\]

NO at high concentrations generally scavenges O\textsubscript{3}, which results in NO\textsubscript{2} formation. Additionally, high NO\textsubscript{2} levels redirect the initial oxidation step of VOCs, preventing net formation of O\textsubscript{3}. Owing to these reactions, if the NO\textsubscript{2} concentration decreases, the O\textsubscript{3} concentration can increase in a phenomenon called the VOC-limited regime, where controlling the emission of organic compounds is a more efficient method of reducing the O\textsubscript{3} peak at low VOC/NO\textsubscript{2} ratios. By contrast, meteorological processes can decreases the NO\textsubscript{2} concentration more rapidly than the VOC concentration, and consequently the VOC/NO\textsubscript{2} ratio is high. The chemistry tends toward the NO\textsubscript{2}-limited case, and NO\textsubscript{2} reduction is considered more effective for reducing the peak O\textsubscript{3} concentration (European Environment Agency, 2008). However, Kramp et al. (1994) and Flocke et al. (1994) indicated that the photochemistry in urban plumes proceeds faster than previously assumed. Oxidation of VOCs contributes to more ozone formation over a shorter time period and to faster removal of NO\textsubscript{2}. Hence, a regime in which ozone formation is controlled by the NO\textsubscript{2} concentration is reached more quickly than previously thought (Borrell et al., 1995). In addition to the effect on the O\textsubscript{3} peak of emission of its precursor, the meteorological conditions also have an important effect on the O\textsubscript{3} concentration. Liu et al. (1994) suggested that larger temperature increases, a high percentage of low cloud cover, lack of precipitation, clockwise changes in wind direction, and a high percentage of low wind speeds are favorable meteorological conditions contributing to O\textsubscript{3} formation. Under these stagnant conditions, pollutants generally accumulate over the city, in particular over cities located in basins surrounded by mountains. Additionally, the impacts of meteorological conditions on O\textsubscript{3} in Jakarta were studied by Permadi and Oanh (2008). They suggested that the synoptic meteorological conditions such as high-intensity solar radiation, high temperature, and light winds are favorable for peak O\textsubscript{3} concentrations.

In Southeast Asia, fire emissions from biomass burning is an important source that releases the O\textsubscript{3} precursors NO\textsubscript{2} and VOCs (Sonkaew and Mac- atanyag, 2015). The peak months of biomass burning in Southeast Asia are typically February and March (Chang and Song, 2010). Biomass burning can have both natural and anthropogenic causes (Yadav and Devi, 2018). Fire emissions also provide an additional atmospheric pathway for ozone production (Chen et al., 2017). Further, fire emissions affect atmospheric chemistry via several processes such as physical and chemical transformations, as well as the dilution and release of chemical oxidants. Photochemistry plays a key role in providing O\textsubscript{3} sinks and sources. The O\textsubscript{3} budget is thus sensitive to the photochemical reactivity of VOCs and NO\textsubscript{2}. Under short-term regulatory measures, reduction of anthropogenic VOC emissions is efficient in decreasing O\textsubscript{3} concentrations. However, this approach only changes the VOC–NO\textsubscript{2}–O\textsubscript{3} reaction mechanism from NO\textsubscript{2}-dependent to VOC-dependent, where VOCs become a limiting factor (Xue et al., 2017). Fire emissions clearly increase the O\textsubscript{3} burden via the resulting photochemistry. As reported by Pfister et al. (2006), who used the chemistry transport Model for Ozone and Related chemical Tracers (MOZART-4) to examine ozone production due to boreal forest fires in Alaska and Canada in summer 2004, revealed that the fire emissions increased the O\textsubscript{3} concentration by approximately 7%–9% over Alaska and 2%–3% over Europe. Furthermore, a study of the tropospheric ozone distribution using the Goddard Earth Observing System (GEOS) Chemistry 3-D global tropospheric chemical transport model with in situ and satellite observations found that decreasing biomass burning emissions can decrease tropospheric ozone by approximately 8% (Parrington et al., 2012). The Transport and Chemical Evolution Over the Pacific campaign, which was conducted during February–April 2001 (Kondo et al., 2004) found that reactive nitrogen (NO\textsubscript{x}, PAN, HNO\textsubscript{3}, and nitrate) and O\textsubscript{3} are the main chemical species produced by biomass burning in this region. Further, Amnuaylojaroen et al. (2014) suggested that biomass burning contributes considerably to air pollution in Thailand and Southeast Asia. It makes substantial contributions of 29% and 16% of O\textsubscript{3} and CO, respectively, during the high-emission period in March compared to those in the low-emission period in December. As much as 70% of biomass burning in this region occurs in Myanmar and Laos, as reported by Punansompong and Chantara (2018) and Kiattwattanacharoen et al. (2017).}

VOCs are known to be the main contributor to O\textsubscript{3} formation. There are few studies of the role of VOCs in O\textsubscript{3} pollution, in particular few modeling studies. For example, Xue et al. (2017) investigated the distribution and role of VOCs in O\textsubscript{3} formation in the typical industrial city of Baqiao in Northwestern China by monitoring the concentrations of related chemical species. They collected air samples at three urban sites. Their results showed that alkenes and aromatics from industry and traffic were the main contributors to the photochemical reactivity. The potential contribution of VOCs to O\textsubscript{3} formation was also studied by Olumayede (2014), who collected data on 16 VOC species from nine sites in an urban area.
Finally, the effect of biomass burning emissions on VOCs and its roles in O3 formation were investigated by comparison to several data sets. Emission data and observations used for model evaluation. Section 2 and then describes the data used in this work, such as the input emission data and observations used for model evaluation. Section 3 reports the performance of the model by comparison to several data sets. Finally, the effect of biomass burning emissions on VOCs and its role in O3 pollution are analyzed in Section 4. We hope that these findings will provide scientific information that supports the planning of emission reductions.

2. Methodology

2.1. Model configuration

We used the online coupled atmospheric and chemistry model WRF-CHEM, version 3.8.1 (Grell et al., 2005), to simulate the meteorological conditions and air pollutant concentrations in March 2014. WRF-Chem is a regional air quality model that shares a physical scheme with the WRF model. It has been developed to study several topics in air pollution and atmospheric chemistry research, and it is also used for operational air quality forecasting. In this study, the model was configured with one domain having a horizontal resolution (grid spacing) of 50 km. In addition, the model was set to have 30 vertical levels up to 50 hPa. The outer domain (d01) covers the entire upper mainland of Southeast Asia and some areas of East and South Asia, such as southern China and eastern India, as shown in Fig. 1. This spatial domain was chosen because Southeast Asia is influenced by the East Asian monsoon, which carries air masses from high latitudes into this region, and by transboundary transport of emissions from countries on the west border, such as Myanmar and Laos, whereas the inner domain (d02), with a horizontal resolution (grid spacing) of 10 km, covers northern Thailand. The WRF-CHEM configurations are shown in Table 1. To resolve water vapor, cloud, and precipitation processes, the model was configured using the Thompson scheme (Thompson et al., 2004). Here, the subgrid-scale process for solving convection is the Kain–Fritsch scheme (Kain, 2004). It uses a cloud model with updrafts and downdrafts, and considers the impacts of detrainment and entrainment on cloud formation. The similarity theory scheme was also used to simulate the thermal gradient over the surface, which is responsible for the friction velocities and wind on surfaces (Paulson, 1970; Dyer and Hicks, 1970; Webb, 1970; Zhang and Anthes, 1982). The planetary boundary layer was configured using the Mellor–Yamada–Janjic scheme (Janjic, 2002), and the Noah land surface model (Chen and Dudhia, 2001) was used to represent the heat and moisture fluxes on land. The initial meteorological and boundary conditions were generated from the Final Analysis Data output, which has a 1° x 1° grid spacing and a temporal resolution of 6 h (https://rda.ucar.edu/datasets/ds083.2/). To reduce the effect of the initial conditions, model spin-up was run for February 15–28, 2014. In the WRF-Chem run, the MOZART mechanism was used to represent the gas-phase chemistry (Emmons et al., 2010). The fast-TUV scheme, which modifies the photolysis rate depending on the presence of clouds and aerosols, was used to calculate the photolysis rate in the model run (Tie et al., 2003). Further, dry and wet deposition of gases were modeled using the resistance methods of Wesely (1989) and Neu and Prather (2012), respectively. In addition, the Model of Emissions of Gases and Aerosols from Nature (MEGAN) was used to estimate biogenic emissions (Guenther et al., 2006).

2.2. Emission data

We included both the anthropogenic and biomass burning emission inventories in the simulations. The biomass burning emissions were taken from the Fire INventory (FINN) from the National Center for...
Atmospheric Research (NCAR) following Wiedinmyer et al. (2011). FINN is a global biomass burning emission inventory and provides daily data with 1 km grid resolution. It estimates the trace gas and aerosol emission from any open burning, i.e., wild fires, agricultural fires, biofuel use, and trash burning. The FINN output has global coverage with high temporal and spatial resolution for key chemical species such as formaldehyde and methanol. The biomass burning emissions were also estimated from the MODIS fire and thermal anomalies. Several factors such as the assumed area burned, land cover maps, biomass consumption estimates, and emission factors contribute to the uncertainties in the model simulations.

The Emission Database for Global Atmospheric Research Hemispheric Transport of Air Pollution (EDGAR-HTAP) was used to simulate anthropogenic emissions. EDGAR-HTAP provides monthly data on global anthropogenic emissions at a resolution of 0.1°/66° in a grid with 72 vertical layers at various temporal resolutions, such as hourly, daily, and monthly. Here, we used the monthly data for the 2 m temperature for model evaluation (Rienecker et al., 2011).

Fig. 2 shows the average spatial distributions of biomass-based and anthropogenic CO and NO emissions in March. The area was separated into three zones (Fig. 1); zone 1 covers mainly India, zone 2 covers upper Southeast Asia, and zone 3 covers some areas of southern China. Biomass burning is the main source of CO and NO emissions in March, especially in zone 2, which shows approximately 250 mol/km²/h of CO and 5 mol/km²/h of NO from biomass burning, as shown in Table 2. In addition, zones 1 and 3 also showed high CO and NO emissions from biomass burning, which accounted for approximately 40% of the total emissions in both areas.

### Table 2

| Area   | Energy | Industry | Residence | Transportation | Biomass |
|--------|--------|----------|-----------|----------------|---------|
|        | CO     | NOₓ      | CO        | NOₓ            | CO      | NOₓ |
| Zone1  | 0.09   | 0.08     | 0.37      | 0.01           | 0.79    | 0.02 |
| Zone2  | 0.01   | 0.02     | 0.13      | 0.02           | 0.57    | 0.01 |
| Zone3  | 0.03   | 0.13     | 1.31      | 0.14           | 1.09    | 0.02 |

**2.3. Data used for evaluation**

The reanalysis data from the Modern-Era Retrospective Analysis for Research and Applications (MERRA) product was used for model evaluation. The dataset was generated using the GEOS Model Data Assimilation System version 5 for atmospheric data assimilation. This system provides several types of atmospheric data, including precipitation and temperature, with a spatial resolution of 0.5° × 0.66° in a grid with 72 vertical layers at various temporal resolutions, such as hourly, daily, and monthly. Here, we used the monthly data for the 2 m temperature for model evaluation (Rienecker et al., 2011).

The Tropical Rainfall Measuring Mission (TRMM) satellite data used to evaluate the precipitation simulations in this study. It was developed by a joint mission between NASA and the Japan Aerospace Exploration Agency to better understand the distribution and variability of precipitation over the tropics. The TRMM dataset provides hourly, daily, and monthly precipitation data with a spatial resolution of 36 km over the tropical region. The high-resolution precipitation data from TRMM were acquired using the data from its microwave imager, and the data were corrected using surface precipitation gauges (Huffman et al., 1997).

The Ozone Monitoring Instrument (OMI) Level-3 Global Gridded NO2 data are generally provided by the NASA Goddard Earth Sciences Data and Information Service Center (GES DISC). Its coverage of NO2 is global and has a spatial resolution of 13 km × 24 km. The tropospheric NO2...
column retrieval algorithm follows Bucsela et al. (2006), who used the differential optical absorption spectroscopy methodology, air mass factors, and typical NO2 profiles from chemical transport models to obtain the vertical column density. To evaluate the modeled NO2 profile, we compared the tropospheric NO2 column from the OMI Level-3 Global Gridded NO2 data product with WRF-Chem NO2 columns that were adjusted using the averaging kernel and a priori information provided with the data product (e.g., Emmons et al., 2004; Amnuaylojaroen et al., 2014), as follows:

\[
x = Ax + (I - A)x_0
\]

where the retrieved mixing ratio is expressed in terms of a linear combination of the real atmospheric profile \(x\) and a priori information \(x_0\), balanced according to the averaging kernel \(A\) (\(I\) is the identity matrix).

From this result, the following was calculated:

\[
\text{Mean Bias} = \bar{M} - \bar{O}
\]

\[
\text{Index of Agreement, IOA} = 1.0 - \frac{\sum_{i=1}^{n} (O - M)^2}{\sum_{i=1}^{n} [M - \bar{O}]^2}
\]

where \(O\) is the observational data, \(M\) is the model data, and \(n\) is the number of model and observational data points. The mean absolute error (MAE) is calculated as

\[
\text{Mean Absolute Error, MAE} = \frac{\sum_{i=1}^{n} |M - O|}{n}
\]

Ground-based measurements in Thailand are made by the Thai Pollution Control Department (PCD). They provide hourly surface concentrations of six chemical species: CO, O3, SO2, NO2, PM10, and PM2.5. Most of the observation instruments use Teledyne Advanced Pollution Instrumentation Model 400 (http://www.teledyne-api.com/products/400e.asp) for O3 and NO2 and Teledyne Advanced Pollution Instrumentation Model 300 (http://www.teledyne-api.com/products/300e.asp) for CO. The O3 and CO measurements have low detection limits of approximately 0.6 and 40 ppbv, respectively (Amnuaylojaroen et al., 2014).

3. Results and discussion

3.1. Model evaluation

Fig. 3 compares the model precipitation output with the TRMM data (Fig. 1a), the 2 m temperature and wind speed output with the MERRA data (Fig. 1b and c), and the NO2 tropospheric column with the OMI data (Fig. 1d). The monthly averaged precipitation from the model generally agrees fairly well with the TRMM output in March 2014; however, the precipitation on land was underestimated by approximately 1 mm/day (e.g., Thailand has 1–2 mm/day less precipitation than the TRMM data). The low precipitation is due to the coarse model resolution of 50 km, which makes it difficult to capture the convection process well. As discussed in Amnuaylojaroen et al. (2014), the precipitation in this region is influenced by convection, which is controlled by mesoscale processes. The model generally simulated the temperature moderately well compared to the MERRA data. The WRF model slightly underestimated the temperature over Southeast Asia, especially in Thailand, Myanmar, and Laos, by 1–3 °C. The modeled wind speed exceeds the MERRA data by ~1–2 m/s on land and is ~3–5 m/s higher than the reanalysis output on the South China Sea. The WRF-CHEM output generally underestimated the magnitude of the NO2 tropospheric column over Southeast Asia by \(1 \times 10^{15}\) to \(3 \times 10^{15}\) molecules/cm²/s; however, the model captured the NO2 tropospheric column well in most areas of Thailand and Myanmar. Some parts of India also showed a lower NO2 tropospheric column compared to the OMI data. As discussed in Amnuaylojaroen et al. (2014) and Ghude et al. (2013), the model’s underestimation of NO2 was likely affected by
the low anthropogenic NOx emission. Another plausible reason is the error of the model resolution, which must be comparable to or smaller than the spatial variability of NO2 to accurately model NO2-OH feedback in the tropospheric NOx chemistry, as discussed in Martin et al. (2003) and Valin et al. (2011).

The modeled output from the inner domain, i.e., the 2 m temperature, precipitation, NO2, CO, and O3 output, was compared to datasets from several types of observation, i.e., satellite, reanalysis data, and ground-based measurement from the Thai PCD, as shown in Table 3. To clarify the model capability, statistical metrics such as the IOA, mean bias, and MAE were used for model evaluation. The WRF-Chem simulations agree fairly well with the ground-based observations. The monthly mean 2 m temperature and precipitation results are acceptable, with IOAs of 0.78 and 0.76, although the model slightly overpredicted the temperature (by ~0.39°C) and the precipitation (by ~0.22 mm/day). Overall, most of the chemical species from the model were underestimated compared to the observations. Additionally, WRF-Chem predicted the chemical species (O3, NO2, and CO) moderately well, with IOA values of approximately 0.5. As discussed in Amnuaylojaroen et al. (2014), the aggregated coarse-resolution data for biomass burning emissions are used to calculate all chemical species via the plume rise model in WRF-Chem. These calculations may capture much of the thermal buoyancy of fires that lifts these species to high altitudes.

3.2. VOC–NOx–O3 system in upper Southeast Asia

In this section, we analyze the role of individual VOCs in O3 pollution over upper Southeast Asia. The impacts of biomass burning emissions on VOCs, which control the surface O3, is also examined. Fig. 4 shows the difference between WRF-CHEM simulations including anthropogenic, biomass, and biogenic emissions and WRF-CHEM simulations excluding biomass burning emissions. The biomass burning emissions are responsible for increasing O3 by approximately 0.5–1.5 ppmv over upper Southeast Asia, whereas they account for an O3 increase of approximately 0.5 ppmv in some areas of India and southern China. The VOC and NOx concentrations are generally not directly proportional to the final O3 concentrations. To control the peak of O3 formation, the relationships of VOCs and NOx to O3 were determined using the indicator species HCHO/NOy established by Sillman (1995). According to the hydrocarbon-sensitive chemistry in the models, for HCHO/NOy < 0.28, ozone production is VOC-limited; otherwise, it is said to be NOx-limited. By examining the ratio of formaldehyde (HCHO) to NOy (= NOx + NO3 + N2O5 + PAN + HNO3) in March 2014.
\[ \text{N}_2\text{O}_5 + \text{PAN} + \text{HNO}_3 \] (Fig. 5), we find that the net \( \text{O}_3 \) production regime over upper Southeast Asia is clearly \( \text{NO}_x \)-limited. In \( \text{NO}_x \)-limited areas, the \( \text{O}_3 \) concentration is insensitive to both decreases in VOCs at constant \( \text{NO}_x \) and to the VOC composition.

\( \text{NO}_x \) generally plays a crucial role in \( \text{O}_3 \) formation via \( \text{NO}_2 \) photolysis. Further, \( \text{O}_3 \) is produced by oxidation of VOCs in the presence of \( \text{NO}_x \) and sunlight. The effect of VOCs on surface \( \text{O}_3 \) is analyzed via the radical production reaction rates in Fig. 6. The production of peroxy radicals from OH oxidation of CO and nine VOC chemical species (HCHO, CH\(_4\), CH\(_2\)OOH, C\(_2\)H\(_8\), C\(_2\)H\(_6\), C\(_3\)H\(_8\), CH\(_3\)OOH, BIGENE, and BIGALK) is based on the MOZART-4 mechanism in the WRF-Chem model. These chemical species were analyzed to determine which of them dominate the surface \( \text{O}_3 \) chemistry. Note that BIGENE and BIGALK represent lumped alkenes and alkanes, whereas the MOZART mechanism uses the name “aldehydes” (HCHO = CH\(_2\)O) (Emmons et al., 2010). The production of peroxy radicals shows that CO and BIGENE generally dominate the reaction rate by approximately \( 5 \times 10^{-3} \) - \( 3 \times 10^{6} \) molecules/cm\(^3\)/s and \( 1 \times 10^{-5} \) - \( 2.5 \times 10^{6} \) molecules/cm\(^3\)/s, respectively. These results show that CO and BIGENE are the main VOCs contributing to surface \( \text{O}_3 \) formation by atmospheric oxidation in upper Southeast Asia. Additionally, biomass burning emissions increase both the CO and BIGENE reaction rates to approximately \( 0.5 \times 10^{6} \) - \( 1 \times 10^{6} \) molecules/cm\(^3\)/s, respectively. These results show that biomass burning emissions potentially contribute greatly to CO and BIGENE, which control surface \( \text{O}_3 \) formation in upper Southeast Asia.

4. Conclusion

We first applied a regional atmospheric chemistry model to study the effect of VOCs on surface \( \text{O}_3 \) formation in upper Southeast Asia during an intense biomass burning episode. The model can be used to analyze the contributions of VOCs to surface \( \text{O}_3 \) formation with acceptable accuracy. By comparing the model results to TRMM, MERRA, and OMI datasets, we found that the model generally agrees well with the precipitation, 2 m temperature, and wind data. However, the magnitude of the \( \text{NO}_2 \) tropospheric column is generally underestimated in most areas of upper Southeast Asia. A comparison of WRF-CHEM simulations with and without biomass burning indicated that biomass burning emissions are responsible for increasing \( \text{O}_3 \) by approximately 1 ppmv in upper Southeast Asia. However, the underestimation of the modeled \( \text{NO}_2 \) tropospheric column likely affected the surface \( \text{O}_3 \) simulation in the model, especially because this region is \( \text{NO}_x \)-limited. If the underestimation of \( \text{NO}_2 \) is corrected, the model would probably simulate the surface \( \text{O}_3 \) concentrations more accurately, which might increase the surface \( \text{O}_3 \) difference. An analysis of the surface peroxy radical production reactions of nine VOCs and CO showed that CO and BIGENE are the two main chemical species that produce \( \text{O}_3 \) by atmospheric oxidation in upper Southeast Asia. We also found that biomass burning emissions play a key role by increasing both the CO and BIGENE reaction rates and thus tend to increase the production of \( \text{O}_3 \) in upper Southeast Asia.

Declarations

Author contribution statement

Teecharai Amnuaylojaroen: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.
Ronald C. Macatangay: Analyzed and interpreted the data; Wrote the paper.
Suratsawadee Khodmanee: Contributed reagents, materials, analysis tools or data.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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