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Impact of biogenic volatile organic compounds on ozone production at the Taehwa Research Forest near Seoul, South Korea

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HIGHLIGHTS

- We presented trace gas observation results in the suburban Seoul Metropolitan Area.
- We found BVOCs are dominant OH chemical sinks.
- WRF-Chem modeling results show that BVOCs are important ozone precursors.

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ABSTRACT

The importance of biogenic volatile organic compounds (BVOCs) in understanding of air-quality and climate on regional to global scales has been highlighted in a number of modeling and observational studies. At the same time, another important emerging research topic in atmospheric chemistry is the regional and global impacts of fast growing East Asian megacities. These two research topics must be integrated in order to adequately understand and address air quality challenges emerging from Eastern Asian megacities surrounded by planted or natural forest areas. We present initial measurement results for May, June and September 2011 from the Taehwa Research Forest (TRF) which has been developed to serve as a long term observatory for investigating biosphere–atmosphere interactions at the edge of the Seoul Metropolitan Area (population of ~23.5 million). The comprehensive measurement datasets of ozone and its precursors such as CO, NO_x, SO₂ and VOCs shows that high ozone episodes in the suburban site could not be explained by just anthropogenic pollutants alone. In addition, isoprene (C₅H₈) and monoterpenes (C₁₀H₁₆) were observed as two of the most important OH chemical sinks inside of the forest canopy. In order to understand the impacts of these BVOCs on ozone and related photochemistry, we conducted model sensitivity simulations using a coupled meteorology–chemistry model (WRF-Chem) for conditions including with and without BVOC emissions. The modeling results suggest that BVOC emissions could enhance regional daytime ozone production from 5 to 20 ppbv. The observed temporal variations in ozone correspond well with the variations in BVOCs, which likely reflects the influence of BVOCs on ozone formation. These findings strongly suggest that interactions between anthropogenic pollutants and BVOCs must be understood and quantified in order to assess photochemical ozone formation in the regions surrounding East Asian megacities.

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1. Introduction

Over the past three decades, the importance of biogenic volatile organic compounds (BVOCs) for tropospheric photochemistry has

been intensively studied. They are expected to have a major global role since BVOC emission is estimated to be much higher than anthropogenic volatile organic compound (AVOC) emission (Guenther et al., 2006; Goldstein and Galbally, 2007). The global dominance of BVOC is not only just in the total amount of emissions but also because BVOC reactivity with oxidants in the troposphere (e.g. hydroxyl radical (OH), ozone, and nitrate radical (NO₃)) is usually much higher than for AVOCs. The reactivity contributions from ambient BVOC concentrations is often much higher than that

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of AVOCs even in urban areas (e.g. the Southeastern U.S. region; Chameides et al., 1988). Therefore, photochemistry of BVOCs in urban environments should be thoroughly studied to address photochemical ozone and secondary organic aerosol (SOA) formation. This consideration is especially critical to study air quality of Asian megacities where urban areas are often near forested regions. In the absence of urban air pollution, BVOCs and natural sources of NO_x maintain a level of oxidation capacity that effectively removes reactive toxic gas species and greenhouse gases in the atmosphere (e.g. methane). Excess NO_x emissions from human activities can upset the natural balance and cause secondary photochemical pollution. The elevated level of ozone is harmful to human respiratory systems (Patz et al., 2005). In addition, it can cause significant reduction of crop yields (e.g. Heagle, 1989). Finally, tropospheric ozone along with SOA from tropospheric photochemistry interacts with solar radiation to affect regional and global climate (IPCC, 2007).

Recently, a number of studies in East Asia have highlighted the roles of BVOCs in local and regional air quality. Bao et al. (2010) presented a 3-D photochemical modeling study of regional ozone production, in the Kinki region of Japan, with and without BVOC photochemistry and concluded that BVOC emissions from the suburban area can significantly contribute to ozone enhancement in the urban region. Ran et al. (2011) showed VOC measurement results from a suburban site near Beijing and Tianjin, China in the summer of 2010. Although their site is downwind of two megacities, their analysis indicates that biogenic isoprene (C_5H_8) was the second most dominant OH sink among all of the VOC species measured in the afternoon when photochemistry is very active. Therefore, the study concluded that peroxyradicals from isoprene oxidation play an important role in producing ozone in the presence of excess NO_x from the two megacities. Finally, Geng et al. (2011) used a 3-D regional chemistry and transport model constrained by a field measurement dataset to assess the impacts of isoprene on air quality in the Shanghai metropolitan area. Their study showed that isoprene and its oxidation products, transported from upwind forests, contributed to Shanghai ozone formation more than was expected based on a prior assessment without measurement constraints. These recent studies clearly indicate that the potential roles of BVOC in regional photochemistry should be thoroughly studied to effectively address air quality issues in the megacity environment. In the past 10 years, the South Korean government enforced strict regulations to reduce CO , SO_2 and PM_{10} (particulate matter less than $10\text{ }\mu\text{m}$ in diameter), and a significant improvement has been achieved. However, pollution from secondary photochemical products such as ozone and its precursor such as NO_x has been getting worse over the same time (NIER, 2011). In this context, the National Institute for Environmental Research (NIER) of South Korea initiated a comprehensive research project to study the roles of Korean forests in regional photochemistry. The main research activities are conducted at Taehwa Research Forest (TRF), managed by the College of Agriculture and Life Sciences at Seoul National University. The observation and modeling activities are conducted in collaboration with scientists at the National Center for Atmospheric Research (NCAR), Boulder Colorado, U.S.A. under the Gases and Aerosols in Megacities–Biosphere–Atmosphere Interactions (GAMBAI) research initiative designed to investigate human–biosphere–atmosphere interactions and their impacts to air quality and climate on regional to global scales. This paper introduces the TRF site and characterizes photochemistry inside of the forest canopy by presenting measurements conducted in 2011. In addition, WRF-Chem (Weather Research and Forecasting model coupled with Chemistry) model simulations were used to assess the regional role of BVOCs, especially the regional ozone formation potential of isoprene.

2. Methods

2.1. Site descriptions

The TRF site ($37^\circ 18' 19.08'' \text{ N}$ $127^\circ 19' 7.12'' \text{ E}$; 162 m above the sea level) is located $\sim 35\text{ km}$ from the center of the Seoul Metropolitan Area, with a population of 23.6 million (2011). The TRF flux tower is in the middle of a Korean Pine (*Pinus koraiensis*) plantation ($300\text{ m} \times 300\text{ m}$), surrounded by a mixed forest. The height of the tower is 40 m and it is equipped with three air-sampling inlets (4 m, 23 m, and 40 m) along with meteorological sensors (temperature, relative humidity, photosynthesis active radiation (PAR), and total UV radiation) at each sampling height. The observational data that we present in this paper were sampled from the lowest sampling inlet.

2.2. Trace gas analysis

2.2.1. CO , NO , NO_x , NO_y , SO_2 and ozone

A laboratory located $\sim 5\text{ m}$ from the base of the tower contains trace-level gas analyzers (CO , SO_2 , ozone, NO_x , and NO_y) manufactured by Thermo Scientific (Franklin MA, U.S.A.). These trace gases were typically observed at concentrations well above the detection limits except NO dropped below the detection limit when it was titrated by ozone especially during the night when NO_2 photolysis ceased.

2.2.2. VOCs

2.2.2.1. Proton transfer reaction-mass spectrometry (PTR-MS). A high sensitivity proton transfer reaction-mass spectrometry (PTR-MS) system manufactured by Ionicon Analytik GmbH (Innsbruck, Austria) was deployed to measure VOCs at TRF. PTR-MS is a chemical ionization mass spectrometry technique that targets organic compounds and has limited fragmentation so that analytes can be identified based on their molecular masses. As the name suggested, PTR-MS uses H_3O^+ ion as a reagent ion. Any molecule that has a higher proton affinity than water can take the proton (H^+) away from hydronium ions and those protonated ions can be detected by PTR-MS. Most VOCs other than alkanes can be detected by PTR-MS. Therefore, we deployed the PTR-MS system to measure reactive AVOCs and BVOCs (e.g., toluene, benzene, isoprene, monoterpenes, and sesquiterpenes) including oxygenated VOCs (e.g., methanol, acetone, methyl vinyl ketone (MVK) + methacrolein (MACR)) with a two-minute cycling time. Detection limits are estimated to be about 20 pptv (parts per trillion in volume) with a sensitivity of 70 counts ppb^{-1} (Karl et al., 2007). Readers are referred to previous studies (e.g., de Gouw and Warneke, 2007; Blake et al., 2009; Kim et al., 2009, 2010) for more detailed analytical characteristics of PTR-MS.

2.2.2.2. VOC measurements using sorbent cartridges. In principle, PTR-MS quantifies chemical species based on molecular masses of analytes; however, isomers such as the many different monoterpene ($\text{C}_{10}\text{H}_{16}$) and sesquiterpene ($\text{C}_{15}\text{H}_{24}$) species cannot be separated and the PTR-MS can only provide the total for these chemical classes. The monoterpene and sesquiterpene speciation is important because the atmospheric oxidant (OH , O_3 and NO_3) reactivity and SOA yields of these terpenoids can be substantially different. For this reason, sorbent cartridge sampling (Tenax GR and Carbotraph 5TD, Markes Int., Llanstrisant, UK) was frequently conducted at the site. The sampled cartridges were sent to a laboratory at Atmospheric Chemistry Division, NCAR for quantitative analysis. An Agilent 7890A GC/5975C Electron Impact Mass Spectrometer (GC–MS/FID) in conjunction with MARKES Unity1/Ultra thermal desorption system were used for the analysis using

procedures described by Kim et al. (2011). We collected 60 cartridges each in June and September of 2011 over the course of two weeks in the middle of each month. The sampling was conducted between 10 am and 5 pm.

2.3. WRF-Chem simulations

To examine the sensitivity of O_3 photochemistry to BVOCs, we performed model sensitivity simulations using the WRF-Chem (Grell et al., 2005) at 30 km spatial resolution over South Korea and its surrounding areas (Fig. 1). The location of Seoul is also highlighted in the figure. The TRF site is ~ 35 km from the center of Seoul. WRF-Chem is a meteorology-chemistry model developed collaboratively among several groups including NCAR and the U.S. National Oceanic and Atmospheric Administration (NOAA). In this work, we use the mass coordinate version of the model, Advanced Research WRF (ARW) (Skamarock et al., 2005). For the gas-phase chemical mechanism, we use the Regional Acid Deposition Model version 2 (RADM2) (Stockwell et al., 1990). Anthropogenic emissions of NO_x , SO_2 , VOCs, and $PM_{2.5}$ and PM_{10} are taken from the Intercontinental Chemical Transport Experiment – Phase B (INTEX-B) inventory (Zhang et al., 2009). In addition, the 2000 Reanalysis of Tropospheric Chemical Composition (RETRO) (<http://retro.enes.org/index.shtml>) database is used when INTEX-B inventory data are not available. Biogenic emissions are calculated online in the WRF-Chem version 3.2 using the Model of Emissions of Gases and Aerosols from Nature (MEGAN) biogenic emissions module, version 2.04 (Guenther et al., 2006). MEGAN v2.1 maps of isoprene emission factors, leaf area index, and plant functional types were applied. MEGAN includes light, temperature, leaf age, and leaf area index controls over the emissions of isoprene and other biogenic emissions. Dry deposition for trace gases is based on a surface resistance parameterization developed by Wesely (1989). Other parameterizations used in the simulations include Lin et al. (1983)'s microphysics scheme, Grell-Devenyi ensemble cumulus parameterization scheme (Grell and Devenyi, 2002), the Yonsei University Planetary Boundary Layer (PBL) scheme (Hong and Pan, 1996), the Goddard shortwave radiative transfer model (Chou and Suarez, 1994), the Rapid Radiative Transfer Model Longwave Radiation

scheme (Mlawer et al., 1997), and the Noah land surface model (Chen et al., 1997). Initial and boundary conditions for meteorology are from the 1-degree NCEP (National Center for Environmental Prediction) Final Analyses (FNL). Two one-month (June 2011) sensitivity experiments covering the simulation domain were conducted with and without BVOCs. Initial and boundary conditions for the chemical species are based on those of McKeen et al. (2002) that are created from measurements collected onboard previous NASA-sponsored aircraft missions. To minimize the effect of initial conditions on model results, we followed the method used in Jiang et al. (2008) to include two additional days (May 30 and 31) in each simulation to spin-up the initial conditions for atmospheric concentrations of several different emission species.

3. Results and discussion

3.1. CO , NO_x ($NO + NO_2$), SO_2 and ozone analysis

Fig. 2 shows temporal variations of CO , NO , NO_2 , SO_2 and ozone concentrations inside of the forest canopy in June 2011. CO and SO_2 are primary pollutants with different emission sources and chemical lifetimes. The e-folding lifetime of CO (τ_{CO}) is about a month and τ_{SO_2} is about a day. The dominant CO sources in the Seoul Metropolitan Area are emissions from mobile sources (cars) while the dominant SO_2 sources are mostly industrial facilities (NIER, 2011). The previously reported CO concentrations from megacity environments such as Beijing-Tianjin (Ma et al., 2012) and Mexico City (de Foy et al., 2007) were much higher (~ 1 – 2 ppmv) than our observed levels. In addition, the observed CO levels at TRF varied from relatively clean (~ 200 ppbv) to polluted regimes (over 500 ppbv). This shows that TRF is an ideal observational location to explore the roles BVOCs in regional photochemistry for a wide range of anthropogenic influences.

We observed morning NO spikes on most days but with very different magnitudes. Local traffic is a potential source of the morning NO peaks. However, in most cases as shown in Fig. 3, morning NO has two peaks with the earlier peak usually detected before the morning traffic rush hour. Considering NO is usually quickly converted to NO_2 by ozone, the observed NO spikes

Fig. 1. Modeling domain with Seoul and Taehwa Research Forest (TRF) highlighted.

Fig. 2. Trace gas concentration variations at TRF in June 2011.

probably came from fresh sources such as a substantial soil NO emission (Alaghmand et al., 2011), if they were not from anthropogenic sources. Soil NO_x emissions have been well documented and even observed by satellite observations on the regional scale (Bertram et al., 2005). Moreover, Su et al. (2011) reported the process of HONO emissions from soil nitrite mitigated by soil bacteria. The comprehensive assessment of soil emission contribution to regional photochemistry will be investigated in future studies at the TRF site.

The ozone concentrations in June 2011 (Fig. 2) show that there are three very distinct regimes at TRF. In the early part of June, ozone concentrations in the mid-day were observed between 40 and 60 ppbv. In the middle of June, daytime ozone concentrations developed relatively high concentrations, from 80 ppbv to 130 ppbv. Finally, toward the end of June, when the rainy season started in the region, daytime ozone concentrations of 20–40 ppbv were observed. Between the high ozone and low ozone periods, we did not observe any significant difference in CO and NO_x levels, as shown in Fig. 2. To investigate the relative importance of pollution sources (e.g. point or mobile sources) in the high ozone episode, SO₂(ppbv)/CO(ppbv) is plotted on Fig. 2 in the same panel

showing the ozone temporal variation (top panel). Clearly, in early June, SO₂/CO ratios (0.007) are higher than those observed (0.005) in mid-June when the high ozone episode was observed. Considering, SO₂ sources are mostly from power generation, the difference suggests that the high ozone episode in this suburban site was probably caused by mobile sources rather than fresh local point pollution sources near the observation site. A correlation plot between CO and SO₂ during the daytime (11 am–2 pm) with color-coding of ozone concentrations in Fig. 4 also clearly shows that there are several different regimes. This indicates that TRF is a receptor site for several distinct pollution sources which is likely the cause of the different ozone episodes. In the daytime, we consistently observed upslope winds and we did not observe any systematic difference in meteorological parameters between the high and the low ozone episodes.

Fig. 4. A correlation plot between CO and SO₂ concentrations observed in June of 2011 at TRF with color-coding of ozone concentrations. The presented dataset is from the photochemically active period between 11 am and 3 pm.

Fig. 3. NO concentration variation observed in the morning of June 18 showing an NO spike before the rush hour influence around 8 am to 9 am.

Fig. 5. Temporal distributions of VOCs (oxygenated, aromatic, and biogenic) observed at TRF by PTR-MS.

3.2. VOCs analysis using PTR-MS and GC–MS

Long-term VOC measurements in South Korea using automated GC–MS systems have suggested that toluene is the dominant reactive VOC at most monitoring sites operated by NIER (NIER, 2011). Although BVOCs such as isoprene and monoterpenes are expected to be observed in the forest environment, these observation sites have reported BVOC levels under the detection limit (~ 0.1 ppbv) (NIER, 2011). This could be due to the deployment of automated GC systems deployed at the monitoring sites that are not suitable for BVOC measurements. The advanced instrumentation operated at the TRF site provided an opportunity to quantify BVOCs at a suburban site in Korea.

Fig. 5 shows temporal variations of VOCs detected by PTR-MS. Isoprene and monoterpenes were consistently detected at concentrations of 1 ppb or more, in contrast to the NIER automated GC measurement dataset. Daily variations of isoprene show a daily maximum in the afternoon. On the contrary, monoterpene concentrations were highest during the nighttime. These observations indicate that isoprene emission, as expected, is light dependent while monoterpene emissions are temperature dependent at TRF. Strong dependency on light for isoprene emission results in higher ambient concentrations in the daytime. On the other hand, a lack of light dependence and a lower boundary layer

height, and so a smaller mixing volume, during the night causes the higher observed monoterpene concentrations in the nighttime. These observations have been commonly reported by previous studies in other forest environments (e.g. Kim et al., 2010). The pine trees (*P. koraiensis*) surrounding the TRF chemistry tower are expected to emit monoterpenes but lack isoprene emission (Kim et al., 2005). A recent branch enclosure measurement study (Lim et al., 2011) clearly shows that the oak trees (e.g. *Quercus serrata*) near the TRF tower are isoprene emitters. Therefore, the observed isoprene is probably transported from the surrounding oak tree forest.

The monoterpene speciation and relative abundances, analyzed by GC–MS from cartridge sampling in June and September of 2011, differed considerably as summarized in Table 1. The reactive monoterpene, 3-carene, dominated monoterpene concentrations in June of 2011. On the other hand, α -pinene was dominant in the September observations. This finding emphasizes the need for long

Table 1

Monoterpene speciation measured in June and September of 2011. The percentage was calculated from the daytime (10 am–2 pm) GC–MS analysis results.

	May (%)	September (%)
α -Pinene	8	43
β -Pinene	3	11
<i>p</i> -Limonene	2	8
Camphene	86	19
Carene-3	ND	19

Fig. 6. Model simulated biogenic isoprene emissions (black line) and difference in ozone concentrations (red line) between the runs with and without biogenic VOCs in June 2011 over the TRF site. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 7. The WRF-Chem model simulated ozone and isoprene temporal variations. The observed ozone temporal variation is also included for comparison purposes.

term monitoring to assess the effects of changing ambient monoterpene distributions on in-canopy and regional photochemistry.

Based on the measurement dataset, we conducted an OH reactivity (s^{-1}) analysis with reaction constants from NIST Chemistry Webbook (<http://webbook.nist.gov/chemistry/>). OH reactivity is the reciprocal of chemical OH lifetime toward specific chemical species. Therefore, higher OH reactivity from the specific trace gas class indicates that the chemical class may have a greater role in photochemical processes such as ozone production. The calculation results show that OH reactivity from BVOCs is frequently the highest among all of the chemical classes such as AVOCs and inorganic trace gases (CO , NO_x , and SO_2). Considering that a significant portion of South Korea is covered by forest, systematic and long-term monitoring is needed in order to evaluate the roles of BVOC in regional photochemistry.

3.3. WRF-Chem simulation to evaluate the roles of BVOCs in regional ozone formation

The observations at the TRF observatory indicate that BVOC photochemistry can play a significant role in regional ozone formation near the Seoul Metropolitan Area. To quantify this role, we conducted WRF-Chem model simulations with and without BVOC emission. Fig. 6 shows model simulation results over the month of June 2011. Regional scale isoprene emissions are predicted to vary significantly over the month. The peak isoprene emissions were simulated for the mid-month period when high ozone was observed. The WRF-Chem estimates of the ozone increase associated with BVOC photochemistry was also higher, 10–20 ppbv, during this mid-month period. These estimated ozone enhancements are of a similar magnitude as that reported in a previous study that examined the impacts of BVOCs in Eastern China (Wang et al., 2008). In their study, the increase in ozone concentration due to biogenic VOC was up to 30 ppbv at some locations. The model simulated isoprene and ozone concentrations are shown in Fig. 7. The daily maximum (~ 2 ppbv) isoprene predicted by the model (Fig. 7) is similar to the observed values (Fig. 5) at TRF. However, the model predicted ozone concentrations could not capture all of the observed ozone concentration variations. This may reflect the limitation of comparing a ground observation

dataset from one observation site with the results from a regional model. In this context, it should be noted that the previous discussion about the ozone enhancement from BVOC photochemistry refers to the regional scale.

The WRF-Chem simulations indicate that the ozone formation potential in the suburban part of the Seoul Metropolitan area is sensitive to reactive VOC due to the high levels of NO_x . The high ozone episode observed in the middle of June 2011 coincides with the model estimates of higher ozone enhancements from BVOC photochemistry. This result suggests that the observed high ozone episodes may be due to interactions of BVOCs, especially isoprene, with the persistent anthropogenic influences as discussed in the above section.

4. Summary and conclusions

Observations at the TRF observatory near Seoul Korea demonstrate that this site has day-to-day ozone variations that could not be solely accounted for by the conventionally measured anthropogenic trace gases such as CO and NO_x and that there are high BVOC concentrations including isoprene and monoterpenes that dominate the ambient OH reactivity. Furthermore, model simulations suggest that BVOC can enhance daytime ozone concentrations in this region by 5–30 ppbv. These findings strongly suggest that BVOC photochemistry can play a significant role in ozone formation in the suburban region of the Seoul Metropolitan Area. This shows the nonlinear nature of tropospheric photochemistry. In agreement with recent East Asian megacity studies in China and Japan (Wang et al., 2008; Bao et al., 2010; Ran et al., 2011; Geng et al., 2011), observations and model simulations at the TRF site in South Korea demonstrate the importance of natural VOC emissions in regional photochemistry near megacities. The presented observational and modeling results also show that the TRF site near the edge of the Seoul Metropolitan Area is suitable for investigating anthropogenic and biogenic interactions including VOCs and reactive nitrogen compounds (e.g. NO and HONO) and, at times, background photochemistry with minimal influences from anthropogenic pollution depending on the meteorological conditions.

A comprehensive VOC measurement dataset from PTR-MS and GC-MS instrumentation clearly showed that BVOCs were the most

dominant OH chemical sink at the site. Isoprene (C_5H_8) and monoterpenes ($C_{10}H_{16}$) were the two dominant BVOCs detected at TRF. Two measurement datasets from May and September had very different monoterpene speciation.

These results confirm the need for a comprehensive understanding of the role of BVOC photochemistry to address local air quality issues associated with Eastern Asia megacities as well as emerging global air quality issues (Lin et al., 2012). This can be accomplished by continuing the observations presented here to provide a long-term record, extending these observations with with a more comprehensive suite of measurements including a full HO_x budget, short-term campaigns and high resolution regional modeling with a more advanced chemical scheme and improved emission estimates.

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