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Impacts of biogenic isoprene emission on ozone air quality in the Seoul metropolitan area

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HIGHLIGHTS

- The impacts of biogenic isoprene emission on O_3 air quality are numerically examined.
- The increase in O_3 concentration can be 37 ppb due to the biogenic isoprene emission.
- The increase is largely caused by the isoprene emission from the surrounding region.
- HCHO, CCHO, and MPAN transport by local circulations worsens urban O_3 air quality.

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ABSTRACT

The impacts of biogenic isoprene emission on ozone (O_3) air quality during an episode under weak synoptic forcing in the Seoul metropolitan area (SMA), Republic of Korea, are investigated using the Community Multiscale Air Quality (CMAQ) modeling system coupled with the Weather Research and Forecasting (WRF) model. Simulations with different biogenic isoprene emission scenarios show that the impact of biogenic isoprene emission on the daily maximum O_3 concentration is as high as 37 ppb in the Seoul region. The O_3 concentration in the Seoul region is significantly increased by the biogenic isoprene emission from the surrounding region compared to that from within the Seoul region. In addition, the gas-phase chemistry is found to be the most important process for O_3 concentration in the Seoul region in the presence of the biogenic isoprene emission from the surrounding region. While isoprene is not enough to influence O_3 concentration directly due to its short lifetime, the transport of isoprene oxidation products plays a crucial role in increasing O_3 concentration in the Seoul region. Through the process analysis, peroxy methacryloyl nitrate (MPAN) as well as formaldehyde (HCHO) and acetaldehyde (CCHO) is also identified as the important precursor that links biogenic isoprene emission from the surrounding region to O_3 concentration in the Seoul region. After transported by daytime local circulations, the chemistry of isoprene oxidation products contributes to O_3 formation in the Seoul region.

1. Introduction

Ozone (O_3) is one of the most harmful pollutants existing in the urban atmosphere. Long-term exposure to O_3 reduces lung function and increases the risk of asthma in children and nonsmoking adults (McDonnell et al., 1999; WHO, 2003; Lin et al., 2008). In addition, O_3 damages urban trees (Trahan and Peterson, 2007) and degrades rubber and textiles (Lee et al., 1996). O_3 is produced by photochemical reactions in relation to NO_x ($=NO + NO_2$) and volatile organic compounds (VOCs) in urban areas (Haagen-Smit and Fox, 1954). In general, O_3 concentration in urban areas is more sensitive to VOCs concentration than NO_x concentration (Milford et al., 1989, 1994; Sillman, 1999). Over the past few decades, biogenic VOCs as well as anthropogenic VOCs have been recognized as important sources for O_3 formation in urban areas (Chameides et al., 1988).

Isoprene is the most influential species for O_3 formation among biogenic VOCs. The effects of isoprene on O_3 concentration in urban areas have been investigated by many researchers. The contribution of isoprene to O_3 formation becomes significant in a range up to 75% (e.g., Duane et al., 2002) under high air temperature, strong

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solar radiation, and high NO_x level. The effects of isoprene on O_3 concentration are evident and consistent for cities around the world, for example, Vancouver, Canada (Biesenthal et al., 1997), Kaohsiung, Taiwan (Chang et al., 2005), Houston, USA (Li et al., 2007), and Beijing, China (Duan et al., 2008).

The Seoul metropolitan area (SMA) that consists of Seoul, Incheon, and parts of Gyeonggi province is the largest urban area in Korea (population of approximately 22 million). Seoul is surrounded by several mountains to the east, south, and north, and is open to the west. O_3 episodes in the SMA have been studied mostly in association with meteorological aspects. It is known that high O_3 concentration occurs when the sea/land breeze is well developed under weak synoptic forcing regardless of prevailing wind direction (Ghim et al., 2001). It is also known that the recirculation of O_3 precursors has a significant influence on O_3 concentration. Jeon et al. (2012) showed that the recirculation leads to the increase in O_3 concentration by 10.9 ppb when the average NO_x and VOCs concentrations increase by 2.9% and 19.7%, respectively, in an episode of July 2007. Shin et al. (2013) calculated the contributions of VOCs to O_3 formation using four-year observation data and showed the greatest contribution of aromatic compounds.

Despite large biogenic VOCs emissions around the SMA, the impacts of biogenic emissions on O_3 concentration in the area are still poorly understood. Recently, Ryu et al. (2013) examined the impacts of urban land-surface forcing on O_3 concentration in the SMA under weak synoptic forcing using the Community Multiscale Air Quality (CMAQ) modeling system coupled with the Weather Research and Forecasting (WRF) model. They found that one of the important phenomena responsible for increasing O_3 concentration in the presence of urban land-surface forcing is the urban breeze circulation that transports air masses from the mountain area to the urban area in the afternoon. The air masses were found to be characterized by low NO_x and high VOCs levels, resulting in long OH chain lengths. This implies that biogenic isoprene plays a critical role in increasing O_3 concentration in the SMA.

In this study, the impacts of biogenic isoprene emission on O_3 concentration in the SMA are examined using the CMAQ modeling system coupled with the WRF model. To understand how biogenic isoprene emission affects O_3 concentration in the SMA, sensitivity simulations using different isoprene emission scenarios are performed, and then simulation and analysis results are presented and discussed. We focus particularly on pathways involved between biogenic isoprene emission and O_3 concentration.

2. Methodology

2.1. Meteorology model

The WRF model version 3.2 (Skamarock et al., 2008) is used to provide the meteorological inputs for the CMAQ modeling system. For a better representation of urban surface processes, the Seoul National University Urban Canopy Model (SNUUCM) (Ryu et al., 2011) is coupled with the WRF model. Four model domains with horizontal grid sizes of 27, 9, 3, and 1 km are considered. The number of vertical layers is 43, and 16 vertical layers exist below a 2-km height. The lowest vertical grid size is ~35 m. The model is integrated for 72 h from 0000 UTC on 22 June 2010. The National Centers for Environmental Prediction (NCEP) final analysis data are used for initial and boundary conditions. Other experimental setups and the case selected are the same as those in Ryu and Baik (2013).

2.2. Air quality modeling system

The CMAQ modeling system version 4.7.1 (Byun and Schere, 2006) is used in this study. In the air quality simulations, three domains with horizontal grid sizes of 9, 3, and 1 km are considered (Fig. 1a). The default concentration profiles in the CMAQ modeling system are used as initial and boundary conditions in the outermost domain. In the inner two domains, the simulation results in their outer domains are used as boundary conditions. The 29 vertical layers are used in this study, and the lowest 22 layers are the same as those used in the WRF simulation. The Statewide Air Pollution Research Center version 99 (SAPRC-99) chemical mechanism (Carter, 2000) that contains 77 chemical species and 224 chemical reactions and the fifth-generation model CMAQ aerosol module (Foley et al., 2010) are used. The model is integrated for 72 h from 0000 UTC on 22 June 2010, and the results of 0600–2000 LT on 24 June (i.e., from 2100 UTC on 23 June to 1100 UTC on 24 June) are analyzed.

Hourly anthropogenic emission data are estimated for all domains using the Sparse Matrix Operator Kernel Emissions (SMOKE) system (Houyoux et al., 2000). The Model of Emissions of Gases and Aerosols from Nature (MEGAN) (Guenther et al., 2006) is used to estimate hourly biogenic emissions. For example, biogenic isoprene emission is estimated depending on the land-use/land-cover categories (Fig. 1b) and atmospheric conditions. In the SMA, the biogenic isoprene emission rates in forest areas are generally much higher than those in urban areas (Fig. 1c).

To elucidate the impacts of biogenic isoprene emission on O_3 concentration, three additional simulations are performed where biogenic isoprene emissions are removed from different regions: the Seoul region (hereafter, the OUT simulation) (Fig. 1d), outside of the Seoul region (hereafter, the IN simulation) (Fig. 1e), or over the entire domain (hereafter, the NONE simulation) (Fig. 1f). Note that anthropogenic isoprene emission mainly from mobile sources is not totally negligible particularly in urban areas (Park et al., 2011). Except for biogenic isoprene emission, other emissions including the anthropogenic isoprene emission in the additional simulations are set to be identical to those in the control simulation (hereafter, the ALL simulation).

3. Results and discussion

3.1. Model validation

The air quality model is validated for the O_3 concentration in the ALL simulation against observation data measured by UV absorption O_3 analyzers at five air quality monitoring stations. The measured O_3 concentrations are given in parts per billion (ppb) by rounding off to the nearest whole number. The five monitoring stations are located in urban areas in the eastern part of Seoul (Gangdong-gu, Fig. 2a) and in satellite cities located in the southeast (Sungnam, Fig. 2b), the east (Guri, Fig. 2c), the north (Uijeongbu, Fig. 2d), and the south (Anyang, Fig. 2e). These monitoring stations are close to the border between Seoul and Gyeonggi province (Fig. 1f). The diurnal variations of simulated and observed O_3 concentrations on 24 June 2010 are compared (Fig. 2). In the daytime, the maximum O_3 concentrations are slightly underestimated at Guri and Anyang stations and overestimated at Gangdong-gu, Sungnam, and Uijeongbu stations. Despite the site variability, the CMAQ modeling system generally well reproduces the diurnal patterns of O_3 concentration.

3.2. Control simulation

Fig. 3 shows the near-surface O_3 concentration and horizontal wind fields in the SMA at 1200, 1400, 1600, and 1800 LT. The near-surface concentration and wind vector are calculated at the lowest model level. At 1200 LT, the O_3 concentration rapidly increases particularly in the eastern part of the SMA where biogenic