



## Discrepancies between modeled and observed nocturnal isoprene in an urban environment and the possible causes: A case study in Houston



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### ABSTRACT

Air quality simulations were conducted using the Community Multiscale Air Quality (CMAQ) model for nocturnal isoprene in September 2013 using the United States Environmental Protection Agency's (EPA's) National Emissions Inventory of 2011 (NEI, 2011). The results were evaluated against measurements collected at eight Texas Commission on Environmental Quality (TCEQ) Automated Gas Chromatographs (AutoGCs) monitoring stations. The comparisons demonstrated two distinctive behaviors: overestimation before midnight (20:00–23:00 p.m. local time) versus underestimation after midnight (00:00–06:00 a.m.). Analyses identify the uncertainties in nitrate radical (NO<sub>3</sub>) concentration and vertical mixing as the possible minor factors contributing to the underestimation, and the underestimated wind speed as the major factor contributing to the overestimation. Further analysis links isoprene underestimation to the uncertainties in the nocturnal isoprene anthropogenic emissions in the NEI (2011) over industrial areas in Houston. This can be substantiated by the fact that the observed nighttime isoprene concentrations increased when the wind direction veered back from southeast to northeast, placing the stations downwind of industrial facilities. A sensitivity run with adjusted anthropogenic isoprene emissions in the later part of the night (i.e., the emissions were multiplied by the hourly underestimation factors ranging from 3.81 to 14.82) yielded closer isoprene predictions after midnight with slightly improved model mean (0.15 to 0.20 ppb), mean error (−0.10 to −0.04 ppb), mean absolute error (0.18 to 0.15 ppb), root mean squared error (RMSE, 0.27 to 0.25 ppb), and index of agreement (IOA, 0.66 to 0.68). The insignificant improvement was likely due to the uncertainties in the location of the high-peaked anthropogenic emissions. The impacts of the nighttime-adjusted isoprene emissions on the isoprene oxidation products, organic nitrate and ozone, were found to be minimal. This study, however, shows that more in-situ surface nighttime measurement data is critical to constrain the underestimated nocturnal isoprene emissions in Houston.

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### 1. Introduction

Isoprene (C<sub>5</sub>H<sub>8</sub>) is the most abundant biogenic volatile organic compound (VOC) with a global emission rate of 535 Tg yr<sup>−1</sup> (Guenther et al., 2012). It, highly reactive with a short lifetime of ~0.5 h (Jacobson, 2005), plays a major role in tropospheric chemistry and the oxidizing power of the global troposphere (e.g., Wang et al., 1998; Poisson et al., 2000 and Squire et al., 2015). Researchers found that isoprene contributed significantly to ozone formation in urban areas (Kleinman et al., 2002; Solmon et al., 2004; Xie et al., 2008 and Schneidemesser et al., 2011). Isoprene has also been recognized as an important precursor for secondary organic aerosol (SOA) (Claeys et al., 2004 and Kroll et al., 2006). While daytime isoprene has been studied thoroughly (e.g., Wiedinmyer et al., 2006;

Li et al., 2007 and Song et al., 2008), its nighttime counterpart has received little attention, especially from a model performance perspective.

The nocturnal chemistry in urban areas is dominated by the reactions of nitrogen oxides and determines the initial atmospheric chemistry conditions for the next early morning. Millet et al. (2016) observed that isoprene from a nearby forest peaked at night in an urban city and caused high ozone the next morning. The major nighttime radical, nitrate radical (NO<sub>3</sub>), is formed via



and exists in equilibrium with N<sub>2</sub>O<sub>5</sub>. The removal of NO<sub>3</sub> depends on its reactions with VOCs and NO, and on the aerosol uptake of N<sub>2</sub>O<sub>5</sub> (Stutz et al., 2010 and Brown et al., 2011). During the day, NO<sub>3</sub> quickly photolyzes under visible radiation. High uncertainties still remain regarding the nocturnal isoprene oxidation by NO<sub>3</sub>. Model analysis showed that it contributes ~50% of the isoprene nitrates (INs), although

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only accounts for about 6–7% of total isoprene degradation (Horowitz et al., 2007). Those INs terminate the nitrogen cycle by producing secondary isoprene nitrate, forming SOA (1–17%), and depositing to surfaces (Brown et al., 2009 and Mao et al., 2013). Alternatively, INs recycle  $\text{NO}_2$  by dissociation (Xie et al., 2013).

In contrast to biogenic isoprene emissions, anthropogenic emissions dominate during nighttime and daytime in cold seasons (Chang et al., 2014 and Hu et al., 2015). Sahu and Saxena (2015) observed higher nighttime isoprene peaks (mainly from anthropogenic sources) than daytime peak values. Anthropogenic isoprene emissions originate from several sources. For example, previous studies confirmed isoprene emissions in motor vehicle exhaust (McLaren et al., 1996; Reimann et al., 2000 and Borbon et al., 2001). The petrochemical industry manufactures isoprene as an intermediate product for the production of synthetic rubber (Chauvel and Lefebvre, 1989). Additionally, humans exhale isoprene (Buszewski et al., 2007). Wagner and Kuttler (2014) measured unusually high isoprene concentrations near a crowd.

Houston is the fourth most populous city in the United States (US) (<http://www.census.gov/>). The Houston Ship Channel (HSC) area located to the east of Houston hosts numerous petrochemical refineries and plants. The Houston-Galveston-Brazoria (HGB) area has been designated as a marginal ozone nonattainment area by the US Environmental Protection Agency (EPA) under the 2008 National Ambient Air Quality Standards (NAAQS) (<https://www3.epa.gov/airquality/greenbook/hnc.html>). The area experienced twenty-five ozone exceedance days in 2013 with the highest maximum daily 8-hour average (124 ppb) occurred on September 25, 2013 at La Porte, in the neighboring Galveston Bay Area southeast of Houston (<http://www.tceq.state.tx.us>).

This study intends to quantify nighttime isoprene concentration in a unique urban region with a mix of traffic, industrial, and petrochemical emission sources. The National Aeronautics and Space Administration (NASA) Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality (DISCOVER-AQ) aircraft campaign took place in September 2013. Several model studies related to air quality and meteorological issues have been carried out for this period (Choi and Souri, 2015; Czader et al., 2015; Pan et al., 2015; Diao et al., 2016; Li et al., 2016 and Souri et al., 2016). However, to our knowledge, no model evaluation for nighttime isoprene has been conducted so far. This study will contribute a quantitative understanding of the nighttime anthropogenic isoprene emissions which could affect the urban VOC chemistry.

## 2. Modeling and measurements

### 2.1. The modeling system

The Community Multiscale Air Quality (CMAQ) model (Byun and Schere, 2006) was used for this study. The Weather Research and Forecasting Model (WRF) (Skamarock et al., 2008) driven by the

32 km National Centers for Environmental Prediction's (NCEP's) North American Regional Reanalysis (NARR) data (Mesinger et al., 2006) provided nudged meteorological inputs upon the Meteorological Assimilation Data Ingest System (MADIS) and Texas Commission on Environmental Quality (TCEQ) Continuous Ambient Monitoring Stations (CAMS) observations. The model domain centered in Houston (Fig. 1) was built over  $84 \times 66$  grid cells with  $4 \times 4$  km grid resolution. The vertical profile consists of 27 sigma layers extending up to 100 hPa with the first midlevel height at approximately 16 m and 12 layers within 1 km. Lateral chemical boundary conditions were generated from a larger outer 12 km domain with default fixed boundary profiles. Other major WRF and CMAQ configurations are listed in Table 1.

The anthropogenic emissions were prepared by the Sparse Matrix Operator Kernel Emissions (SMOKE) model based on the USEPA's 2011 National Emission Inventory (NEI, 2011), which consists of point, area and mobile source categories. The anthropogenic isoprene is speciated by a source-dependent factor of the total VOC emission. Biogenic emissions were estimated from the Biogenic Emission Inventory (BEIS) model version 3.14 integrated to SMOKE. Biogenic isoprene emissions were zero at night due to their strong dependence on temperature and incident sunlight (Guenther et al., 1995). The reader is referred to Supplementary Figs. S1–S2 for temporal and spatial variations of biogenic and anthropogenic isoprene emissions in and around Houston.

### 2.2. AutoGC and auxiliary measurements

TCEQ operates the network of Automated Gas Chromatographs (AutoGCs) in Houston to monitor a number of VOCs on an hourly basis ([http://www.tceq.state.tx.us/cgi-bin/compliance/monops/agc\\_daily\\_summary.pl](http://www.tceq.state.tx.us/cgi-bin/compliance/monops/agc_daily_summary.pl)). One 40-minute ambient sample is collected and analyzed on-site every hour. The limit of detection (LOD) estimated by TCEQ for isoprene is 0.08 ppb. The average difference between AutoGC and canister data for isoprene concentrations is about  $-25\%$  (Main et al., 2001), suggesting that isoprene concentration measured by AutoGC could be underestimated. Fig. 1 also shows the locations of the eight AutoGC stations: Channelview, Milby Park, Clinton, Hou.DeerPrk2 (DeerPrk2), Cesar Chavez, HRM-3 Haden Road (HRM3), Lynchburg Ferry (Lynchburg) and Wallisville Road (Wallisville). Since these sites are near industrial sources, the sampled ambient VOC levels can vary greatly depending upon wind directions. For example, Clinton is located about 800 m north of the HSC area. High industrial VOC emitters including petroleum refineries and petrochemical plants lie to the south, southeast and east of the monitor, while residential and urban areas to the west and northwest. VOC concentrations are predominantly controlled by industrial emissions when the wind is from south and east, and by automobile emissions when the wind is westerly and northerly (Main et al., 2001). Refer to the Supplementary Fig. S3 for locations of the industrial facilities surrounding AutoGC monitors.

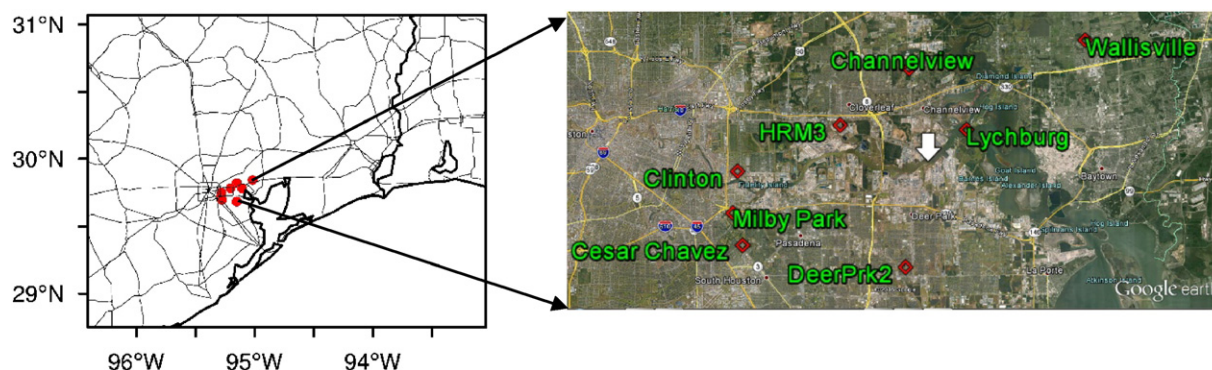


Fig. 1. Model domain. The red dots represent the locations of eight AutoGC sites with a close-up view on the Google map on the right. The white arrow on the Google map points to the HSC area.

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