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Uncertainties of isoprene emissions in the MEGAN model estimated for a coniferous and broad-leaved mixed forest in Southern China

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HIGHLIGHTS
● Local constrained MEGAN tends to estimate isoprene emission reasonably well.
● Considerably high uncertainties were found for isoprene emission using Monte Carlo approach.
● Key uncertainty sources in isoprene emission estimated were identified.

ABSTRACT
With local observed emission factor and meteorological data, this study constrained the Model of Emissions of Gases and Aerosols from Nature (MEGAN) v2.1 to estimate isoprene emission from the Dinghushan forest during fall 2008 and quantify the uncertainties associated with MEGAN parameters using Monte Carlo approach. Compared with observation-based isoprene emission data originated from a campaign during this period at this site, the local constrained MEGAN tends to reproduce the diurnal variations and magnitude of isoprene emission reasonably well, with correlation coefficient of 0.7 and mean bias of 47.5%. The results also indicate high uncertainties in isoprene emission estimated, with the relative error varied from −89.0−111.0% at the 95% confidence interval. The key uncertainty sources include emission factors, \( g_{TLD} \), photosynthetically active radiation (PAR) and temperature. This implies that accurate input of emission factor, PAR and temperature is a key approach to reduce uncertainties in isoprene emission estimation.

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1. Introduction
Atmospheric volatile organic compounds (VOCs) can be from anthropogenic or biogenic sources, and the total VOCs emissions are dominated by biogenic compounds in global scale (Guenther et al., 1995). Accordingly, the measurement and modeling of biogenic VOCs (BVOCs) emissions are essential for understanding regional and global atmospheric chemistry, carbon cycle, and climate change. Isoprene (C\(_5\)H\(_8\)) is the most abundant species (Guenther et al., 1995) in all the identified non-methane biogenic hydrocarbons. Isoprene is very reactive, and can be reacted with hydroxyl radical (OH), ozone (O\(_3\)) and nitrate (NO\(_3\)) to enhance the formation of secondary air pollutants (eg. ozone and secondary organic aerosol) (Carslaw et al., 2000; Carlton et al., 2009) whose impacts may be involved in feedback mechanisms in the Earth’s radiation balance (Fuentes and Wang, 1999). Thus, it is needed to characterize the emission sources of isoprene and quantify the emission flux reasonably (Fuentes and Wang, 1999).

Many studies tried to characterize the sources of isoprene emission and understand emission mechanisms. Generally, forest is considered as the main source of isoprene emission, in particular the broad-leaved trees (Guenther and Wildermuth, 1994). Isoprene is produced in chloroplasts from photosynthetically fixed carbon (Delwiche and Sharkey, 1993) instantaneously. Foliage temperature and intercepted photosynthetically active radiation (PAR) are reported to exert the greatest environmental influence on isoprene emission (Fuentes et al., 2000). Additionally, isoprene emission is
also sensitive to water-stress (Pegorato et al., 2004a), probably caused by stomatal closure. Leaf age plays an important role on controlling isoprene emission. Young leaves do not produce and emit isoprene while mature leaves emit they have received the requisite period of warm temperatures to induce isoprene synthase activity (Kuzma and Fall, 1993; Monsoon et al., 1994; Fuentes and Wang, 1999). Moreover, the increased CO2 concentration has been also proved to inhibit the isoprene emission (Pegorato et al., 2004b).

Based on the known emission mechanisms, numerical emission models have been developed to estimate the isoprene emissions. However, there is high uncertainty associated with different components in these models, including the characteristic of sources, the reasonableness of emission algorithms, the accuracy of emission potentials and driving variables (Guenther et al., 1996a). These uncertainties in biogenic emission estimated were reported varying between a factor of 3 and 5 in the US and Europe (Guenther, 1997; Simpson et al., 1999). These uncertainties can limit the accuracy dramatically and will create a risk of misunderstanding the impacts on air quality. Therefore, uncertainty assessment is very important and required (Smiatek and Bogacki, 2005). In summary, there are three major alternatives to analyze the uncertainties, including the sensitivity analysis, Monte Carlo uncertainty analysis and response surface evaluation (Hanna et al., 2001). The sensitivity analysis has been widely used in the biogenic emission analysis (Wang et al., 2011; Guenther et al., 1999; Huber and Fuentes, 1999) because it is very easy to carry out efficiently. However, the Monte Carlo approach is more efficient than the sensitivity analysis to analyze the uncertainties in modeling systems (Hanna et al., 1998), and has come into the application of quantifying the uncertainties in biogenic emission (Hanna et al., 2005; Zheng et al., 2010b).

The Pearl River Delta (PRD) region, located in the central Guangdong province, is one of the most developed areas in China. Air quality in this region has been deteriorating in recent years. Fine particulates and ozone are the major air pollutants in this region, with high concentrations frequently occurring in fall (Zhang et al., 2008; Zheng et al., 2010a). The PRD region is influenced by a subtropical monsoon climate, showing the characteristics of high temperature and radiation in most seasons. The vegetation in this region is mainly subtropical evergreen forest containing some high isoprene emitters (Klinger et al., 2002). According to the regional isoprene emission inventories, the annual emission of isoprene over the PRD is higher, compared with the reported mean isoprene emission for the whole China and that for North America (Zheng et al., 2010b; Wang et al., 2011; Tie et al., 2009; Guenther et al., 2000). Moreover, local observations also reveal that isoprene emission contributes much to the formations of surface ozone and secondary organic aerosol (Tang et al., 2007; Ding et al., 2012). It is important to estimate isoprene emission reasonably and quantify the related uncertainties in such a typical region. Although a few studies have begun to pay attention to the uncertainties in isoprene emission estimated in this region (Zheng et al., 2010b; Wang et al., 2011), none of them has analyzed the uncertainties and evaluated the modeled results with observed data.

MEGAN (Model of Emissions of Gases and Aerosols from Nature) is the most widely used model for projecting global and regional trends in biogenic emissions (Niinemets and Monson, 2013). In the present study, MEGAN will be constrained with local measurements and evaluated with observation-based data originated from a campaign conducted during fall season (25th Nov. to 1st Dec.) 2008, to determine whether MEGAN can reasonably estimate the isoprene emission from the Dinghushan forest. Thereafter, the uncertainties associated with modeled emissions will be quantified using Monte Carlo approach. Section 2 describes the methodology, including the study area, measured approach, available data and emission model. Section 3 presents model evaluations and uncertainty analysis. Finally, Section 4 draws the conclusions.

2. Methodology

2.1. Study area and isoprene ambient measurement

As shown in Fig. 1 (left panel), DBR is located in the northwest of PRD. The annual average precipitation is 1927 mm, and the annual mean temperature is 21.4 °C with the maxima of 31 °C and the minimum of 0.2 °C (Zhou et al., 2007). The DBR covers an area of 11.6 km², and has three major forest types, including the pine forest, the mixed pine and broad-leaved forest and the broad-leaved forest. The distributions of different forests can be seen in Fig. 1 (right panel). The study site (112.53°E 23.17°N) is in the center of DBR (Fig. 1, right panel), which is surrounded by Cryptocarya concinna, Schima superba, Castanopsis chinensis and Pinus massoniana primarily (Wang et al., 2007).

Whole air samples were collected in the DBR every 2 h in daytime (8:00—18:00 LT) during the campaign, using 2-L electro-polished stainless steel canisters. During field sampling, an Entech’s restrictive sampler (Part No. 39-RS-3, Entech Instruments Inc., CA, USA) was adopted to allow each canister to be filled in about 60 min. All the samples were analyzed at the Guangzhou Institute of Geochemistry (GIG), Chinese Academy of Sciences. 58 VOC species were determined, including isoprene. Detailed sampling and chemical analysis for samples has been reported by Zhang et al. (2013).

2.2. Using MEGAN for estimating isoprene emission

The latest version of MEGANv2.1 was used to predict the isoprene emission during the campaign. MEGAN isoprene emission is based on a simple mechanistic model (Equation 1), which considers the major processes driving variations in isoprene emission (Guenther et al., 2012).

\[ E = \gamma \cdot \varepsilon \cdot \rho \]  

(1)

where \( E \) is the isoprene net emission rate (\( \mu g \ m^{-2} \ h^{-1} \)), \( \gamma \) is the activity factor for isoprene emission, \( \varepsilon \) is the canopy-scale emission factor (\( \mu g \ m^{-2} \ h^{-1} \)), \( \rho \) is a factor that accounts for chemical production and loss of isoprene in the vegetation canopy.

The activity factor \( \gamma \) accounts for emission responses to radiation (\( \gamma_0 \)), temperature (\( \gamma_T \)), leaf age (\( \gamma_A \)), soil moisture (\( \gamma_{SM} \)), leaf area index (\( \gamma_{LAI} \)) and CO2 inhibition (\( \gamma_C \)). Eq. (2) shows the algorithm for \( \gamma \), in which \( \gamma_{CEF} \) is the canopy environment coefficient with the value of 0.57 for the canopy environment model used by Guenther et al. (2012).

\[ \gamma = \gamma_{CEF} \cdot \gamma_LAI \cdot \gamma_T \cdot \gamma_A \cdot \gamma_{SM} \cdot \gamma_C \]  

(2)

Particularly, MEGANv2.1 includes a multi-layer canopy model to divide the whole vegetation canopy into many layers and determine the effects of leaf temperature (\( \gamma_T \)) and radiation (\( \gamma_R \)) on emission at each canopy layer respectively. All \( \gamma_T \) and \( \gamma_R \) of different layers are summed up as the total dependence on temperature and radiation (\( \gamma_{T+R} \)) (Equation 3). The total independence on temperature and radiation (\( \gamma_{T+U} \)) for the whole canopy emission is calculated with Equation 4.
where \( n \) is the number of layer divided in canopy, \( \gamma_T \) is the activity factor accounting for temperature and radiation independence at different canopy layer. In this study, we considered the effect of soil moisture and \( \text{CO}_2 \) to be constant by setting \( \gamma_S \) and \( \gamma_C = 1 \) because soil moisture was above the threshold required to impact isoprene emission and \( \text{CO}_2 \) was at the standard condition.

Meteorological data, land cover parameters (including the Plant Function Types and LAI) and emission factor are required to drive the MEGAN calculation.

### 2.2.1. Meteorology

MEGAN requires PAR, air temperature, wind and humidity as driving variables for the emission calculation. For this study, meteorological parameters were observed. All instruments were installed at 31 m above the ground on a flux tower operated by the South China Botanical Garden of the Chinese Academy of Sciences in DBR, including Li190SB (Li-cor) sensor for PAR, HMP45C (Vaisala) sensor for temperature and humidity, and A100R (Vector) sensor for wind speed \( (Yan \ et \ al., \ 2012) \). All the observed meteorological data were incorporated to constrain MEGAN. And the standard MEGAN code was modified to include PAR directly to calculate the isoprene emissions.

### 2.2.2. Plant Function Types (PFTs) and LAI

Based on the forest survey around the study site, the land cover inputs used to parameterize the study site for MEGAN included a PFT composition of 95% broad-leaved trees and 5% needle leaf trees. High resolution, dynamic MODIS LAI data in 2008 was used as the LAI. The seasonal variation of MODIS LAI was comparable to the observed at this site \( (Ren \ et \ al., \ 1994; \ Ren \ and \ Peng, \ 1997) \).

### 2.2.3. Isoprene emission factor

Local studies \( (Bai \ and \ Wang, \ 2001; \ Klinger \ et \ al., \ 2002; \ Tsui \ et \ al., \ 2009) \) have quantified the standard emission factors of isoprene, leaf- or branch-level, for some plant species, including the dominated tree species around the studying site \( (Table \ 1) \). Most of them were measured in DBR. These emission factors were extrapolated to be canopy scale emission factors using the MEGAN canopy environment model, which considered the canopy radiation reduction, the leaf mass \( (Zhou \ et \ al., \ 2011; \ Yan \ et \ al., \ 2006) \) and the

\[
\gamma_T/LD = \sum_{i=1}^{n} \gamma_T \cdot \gamma_P
\]

\[
\gamma_T/LD = \sum_{i=1}^{n} \gamma_T \cdot \gamma_P
\]

### Table 1: Standard emission factors of isoprene for different tree species.

| Tree species       | Emission factor (ug m\(^{-2}\) h\(^{-1}\)) | References        |
|--------------------|-------------------------------------------|--------------------|
| Pinus massoniana   | 13.5                                      | Klinger et al. (2002) |
| Fru                     | 0.5                                       | Klinger et al. (2002) |
| Garcinia oblongifolia | 0.3                                       | Klinger et al. (2002) |
| Picus variolesa       | 1.6                                       | Klinger et al. (2002) |
| Cryptocarya concina   | 55.2                                      | Bai and Wang. (2001) |
| Schima superba        | 0.5                                       | Bai and Wang. (2001) |
| Castanopsis chinensis | 0.6                                       | Bai and Wang. (2001) |
| Sarcosperma laurinum  | 0.8                                       | Bai and Wang. (2001) |
| Eucalyptus robusta    | 11.3                                      | Tsui et al. (2009)  |

| Model parameters | Distribution type | Fitted distribution parameters |
|------------------|-------------------|-------------------------------|
| Activity factor  | \( \gamma_T \)  | Normal                        | Para1 \(^a\) Para2 \(^b\) |
|                  | \( \gamma_S \)  | Normal                        | 0.2 0.2                       |
|                  | \( \gamma_C \)  | Normal                        | 0.3 0.3                       |
|                  | \( \gamma_i \)  | Normal                        | 4.7 0.7                       |
|                  | \( \gamma_m \)  | Normal                        | 4.7 0.7                       |
| Meteorological input | Temperature (K) | Normal                        | 290.3 3.4                    |
|                   | PAR (umol m\(^{-2}\) s\(^{-1}\)) | Normal                        | 741.0 341.1                  |
|                   | Wind speed        | Log-normal                    | 0.5 0.2                      |
|                   | Water mixing ratio | Normal                        | 16.8 2.7                     |
| Vegetation input  | LAI               | Normal                        | 4.7 0.7                      |

\(^a\) Para1: the mean for Normal, the mean of lnx for Lognormal.
\(^b\) Para2: the standard deviation for Normal, the standard deviation of lnx for Lognormal.

LAI for the MEGAN standard condition. The contributions of specific tree species to total tree cover in the Dinghushan forest were used to weight and group the species emission factors for each PFT \( (Wang \ et \ al., \ 2011) \).

### 2.3. Monte Carlo approach for quantifying the uncertainties

Based on the algorithms of MEGAN, the Monte Carlo approach was applied to quantify the uncertainties associated with different model parameters in isoprene emission estimated in this study. Quantification of uncertainties in isoprene emission estimated using Monte Carlo simulation includes two aspects: (1) quantifying the uncertainties related to different model parameter respectively, and (2) propagating the uncertainties during the MEGAN execution. The uncertainties in model parameters, including activity factor, meteorological inputs and vegetation input, were firstly quantified...
with statistical analysis. For emission factor of explicit tree species, the uncertainty ranges were cited from literature (Bai and Wang, 2001; Klinger et al., 2002; Tsui et al., 2009). The probabilistic distributions used to obtain the uncertainties are summarized in Table 2, where the distributions are in accordance with the previous studies (Hanna et al., 1998; Tang et al., 2010; Zheng et al., 2010b). As an example, Fig. 2 shows the fitted distribution and probability band to represent uncertainties in temperature. No information was available to judge the uncertainties associated with the coverage areas for different PFTs and empirical parameters in MEGAN, and they were assumed to be fixed in this study.

3. Results and discussion

3.1. Modeled isoprene emission and its evaluation

The isoprene emission fluxes estimated by MEGAN showed significant diurnal variation with the mean value of 2.4 mg m\(^{-2}\) h\(^{-1}\) in daytime and the maxima at noon (Fig. 3). In order to evaluate the modeled isoprene emission fluxes, a simple box model (Eq. (5)) was adopted to convert the observed isoprene concentrations to observation-based emission fluxes. The simple box model considers the chemical loss, and assumes that (1) the turbulent horizontal fluxes and vertical advection are negligible; (2) the mean mixing ratio has reached a steady state and is homogeneous in space (Guenther et al., 1996b). The mean observed isoprene concentration was 0.3 ug m\(^{-3}\) (113.3 ppt) during the campaign, with the highest value of 0.8 ug m\(^{-3}\) (245.5 ppt) at noon. The diurnal value of mixing layer height used in this model was simulated by WRF at this site during this period.

\[
E = C \cdot Z \cdot L
\]  

(5)

where \(E\) (ug m\(^{-2}\) s\(^{-1}\)) is the emission flux; \(C\) (ug m\(^{-3}\)) is the observed concentration; \(Z\) (m) is the height of mixed-layer capping inversion; and \(L\) (s\(^{-1}\)) is the oxidation rate of isoprene accounting for the chemical loss.

Isoprene can be oxidized by OH and ozone primarily in daytime. The oxidation rate \((L)\) is defined as Eq. (6). The OH and ozone reaction rate coefficients (Atkinson and Arey, 2003), the mean diurnal OH concentration (Lu et al., 2012) and the simultaneous observed ozone concentration at the Chengzhong site, which was about 17 km away from the DBR (Fig. 1, left panel), were employed to estimate the oxidation rate \(L\) of isoprene in this study.

\[
L = [K_{OH} \cdot C_{OH}] + [K_{Ozone} \cdot C_{Ozone}]
\]  

(6)

where \(K_{OH}\) and \(K_{Ozone}\) are reaction rate constants, and \(C_{OH}\) and \(C_{Ozone}\) are mixing ratios of hydroxyl radical and ozone, respectively.

Meanwhile, the representative area for the observed isoprene concentration was also identified by trajectory method, considering the lifetime of isoprene, wind speed and wind direction during the campaign. Conservatively, the observed results represented the mean conditions of 3 km around the observe site, which almost covers the whole DBR.

Comparison of modeled and observation-based isoprene emission fluxes was presented in Fig. 3. MEGAN results corresponded fairly well to the observation-based results with the correlation coefficient of 0.7, and captured the high frequency fluctuations of observation-based fluxes. On average, the model values were about 47.5% higher than observation-based results over the measuring period. This difference can be explained by (1) observation-based fluxes having strong sudden decreases, which are related to the measured approach (Karl et al., 2007); (2) low observation-based fluxes occurring on some days, due to the low mixing layer height and low measured isoprene concentrations on these days. Given the uncertainties in this approach, this comparison indicates that the local constrained MEGAN tends to predict the isoprene emission reasonably well for this location and time.
3.2. Uncertainties in isoprene emission estimated

The means and associated uncertainty ranges for the isoprene emission estimated by MEGAN are summarized in Table 3. All the results were obtained by statistical analysis, after Monte Carlo simulations. As shown in Table 3, the uncertainties varied among the estimated model parameters.

Emission factor of broad-leaved trees (EF_{BT}) showed very high uncertainties, with the relative error of −88.6–111.0% and emission fluxes of 0.8–14.0 mg m⁻² h⁻¹ at 95% CI approximately. This is consistent with the results conducted by Zheng et al. (2010b), which analyzed the uncertainties of isoprene emission estimated by GloBEIS.

Amongst all of the activity factors, γ_{TLI} showed the highest uncertainties with the relative error of −86.1–82.5%, followed by γ_A. In terms of the meteorological inputs, PAR and temperature had relatively high uncertainties, with about −33.4–36.1% and −31.0–48.7% relative error respectively. Humidity and wind speed, which were included for calculating the leaf temperature in the multi-layer canopy model, showed similar uncertainties in the isoprene emission estimated, with the relative error of −11.0–11.0% and −11.1–11.1% respectively. The uncertainties associated with LAI were lower than those associated with PAR and temperature, with −33.6–18.7% relative error.

The uncertainties associated with PAR, temperature and γ_{TLI} showed obvious diurnal variations. Uncertainties associated with PAR increased as PAR increased and reached the maxima at noon, varying between −37.3 and 38.3%. The diurnal variation of uncertainties associated with γ_{TLI} was similar to PAR, with the maxima between −92.6 and 239% at noon. In contrast, the maximal uncertainties associated with temperature occurred at dawn and the values varied between −31.5 and 32.5%. Its related uncertainties at noon ranged from −27.7 to 30.0%.

3.3. Identification of key sources of uncertainties in estimated isoprene emission

Sample correlation coefficients between instantaneous isoprene emission and model parameters in daytime were calculated to identify the key sources of uncertainties in modeled isoprene emission (NARSTO, 2005). Table 4 lists the correlation coefficients between model parameters and isoprene emission estimated. Large correlation coefficients (either positive or negative) imply that the model corresponding parameters contribute significant uncertainties in isoprene emission estimated, and thus should be key uncertainties sources.

EF (either EF_{BT} or EF_{NT}) was found as the most important source of uncertainties in estimating isoprene emission (Table 4), consistent with the results reported by Zheng et al. (2010b). Besides EF, γ_{TLI} was found as another key uncertainty source and would produce high uncertainties in the isoprene emission estimated.

Our results also showed that the isoprene emission estimated was very sensitive to errors in PAR (R = 0.7), indicating that PAR could be an important parameter to estimate isoprene emission. This differed from the conclusions reported by Hanna et al. (2005) and Zheng et al. (2010b). The difference might be ascribed to 1) that Hanna et al. (2005) analyzed the correlation between daily isoprene emission and PAR, in which timescale PAR might not affect isoprene emission as significant as that instantaneously; 2) the PAR with smaller mean and standard deviation in Monte Carlo simulations in the study by Zheng et al. (2010b), resulting in a smaller response of isoprene emission to the change of PAR.

Our results also revealed that temperature was a less significant uncertainty source than PAR (Table 4), although its uncertainty range was comparable with that associated with PAR. LAI was found as a less important uncertainty source, compared with PAR and temperature. This conclusion was consistent with the conclusion reported by Zheng et al. (2010b). Table 4 also showed that humidity and wind speed would introduce relatively low uncertainties.

Leaf age was reported as a critical factor controlling isoprene emission, with −30.7–16.8% relative error in our study, but it was not a significant source of uncertainties. The reason might be attributed to the fact that the campaign was conducted in the fall season and there were only small changes in leaf developmental stage. γ_{TLI} produced very low uncertainties in the estimated isoprene emissions.

4. Conclusions

This study indicates that the local constrained MEGAN tends to predict the isoprene emission from the Dinghushan forest reasonably well, with a mean bias of 47.5% and correlation coefficient of 0.7, during fall 2008. And the mean isoprene emission estimated by MEGAN was 2.4 mg m⁻² h⁻¹ during this period. Considerably high uncertainties for isoprene emission estimated was found using Monte Carlo approach based on MEGAN algorithm, ranging from 0.8 to 14.0 mg m⁻² h⁻¹, with the relative error of −88.6–111.0% at a 95% confidence interval. The emission factors, γ_{TLI}, PAR and temperature were identified as the most important uncertainty sources. LAI and leaf age didn’t affect the isoprene emission estimated significantly in this study. These results imply that accurate input of emission factor, PAR and temperature is a key approach to reduce uncertainties in isoprene emission estimation.

To improve future isoprene emission simulations for this site with the MEGAN, a high priority for further research is more accurate emission factors and observations (simulations) of PAR and temperature. Future work is needed to quantitatively estimate the uncertainties associated with the empirical parameters used to calculate the activity factor γ_{TLI} in MEGAN. More site information at Dinghushan, including the distribution of temperature, PAR and emissions at different depths inside the forest canopy at Dinghushan, are also needed to examine the variability of these empirical parameters and driving variables within the canopy. The work of improving isoprene emission from Dinghushan forest can help improving the regional isoprene emission.

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