

3 OPEN ACCESS

Biogenic isoprene emissions over China: sensitivity to the CO₂ inhibition effect

FU Yu^a and LIAO Hong^b

^aClimate Change Research Center (CCRC), Chinese Academy of Sciences, Beijing, China; ^bSchool of Environmental Science and Engineering, Nanjing University of Information Science & Technology, Nanjing, China

ABSTRACT

Isoprene emissions emitted from vegetation are one of the most important precursors for tropospheric ozone and secondary organic aerosol formation. The authors estimate the biogenic isoprene emissions in China over 2006–2011 using a global chemical transport model (GEOSChem) driven by meteorological fields from the assimilated meteorological data from MERRA. The authors incorporate three different parameterizations of isoprene– CO_2 interaction into the model, and perform three sensitivity simulations to investigate the effect of CO_2 inhibition on isoprene emissions for the period 2006–2011 in China. The annual isoprene emissions rate across China is simulated to be 12.62 Tg C yr⁻¹, averaged over 2006–2011, and decreases by about 2.7%–7.4% when the CO_2 inhibition schemes are included. The CO_2 inhibition effect might be significant in regions where the CO_2 concentration and isoprene emissions are high. Estimates of isoprene emissions can differ depending on the scheme of CO_2 inhibition. According to the results obtained from the sensitivity simulations, the authors find that the CO_2 inhibition effect leads to 5.6% \pm 2.3% reductions in annual isoprene emissions over China. The authors also find that inclusion of CO_2 inhibition can substantially alter the sensitivity of isoprene emissions to the changes in meteorological conditions during the study period.

摘要

陆地植被排放的异戊二烯是对流层臭氧及二次有机气溶胶的形成重要前体物之一。已有研究表明,当CO,浓度超过一定水平时可能使得叶片气孔关闭,对叶片释放异戊二烯产生直接的抑制作用。而这一影响机制在目前大多数异戊二烯排放估算时并没有考虑在内,对其排放的估算仍存在很大的不确定性。本文基于GEOS-Chem及其耦合的MEGAN模式模拟了2006-2011年中国异戊二烯的排放变化。通过引入三种不同CO,抑制作用参数化因子的模拟试验,定量评估了CO,抑制作用对异戊二烯排放的影响及不确定性。结果表明:考虑CO,抑制参数因子后,中国年平均异戊二烯的排放量平均减少了5.6% ± 2.3%。不同参数化方案对排放的抑制程度存在差异。CO,对异戊二烯排放的影响将会改变其对气象条件变化的敏感性,从而影响空气质量。

ARTICLE HISTORY

Received 19 November 2015 Revised 5 January 2016 Accepted 1 April 2016

KEYWORDS

Isoprene emissions; CO₂; inhibition; GEOS-Chem model

关键词

异戊二烯排放;二氧化碳; 抑制作用;模式模拟

1. Introduction

Isoprene is a volatile organic compound (VOC) mainly emitted from terrestrial vegetation, and it makes up the largest fraction of non-methane biogenic VOCs, with an estimated emissions rate of $400-600\,\mathrm{Tg}\,\mathrm{C}\,\mathrm{yr}^{-1}$ at the global scale (Guenther et al. 2006; Arneth et al. 2008). In polluted regions, biogenic isoprene emissions are an important contributor to tropospheric ozone formation in the presence of nitrogen oxides (NO_x), but in remote regions with low-NO_x concentration, isoprene could reduce ozone by sequestering NO_x as isoprene nitrate or by ozonolysis (Fiore et al. 2012). In addition, isoprene acts as a major precursor for secondary organic aerosol (SOA) formation, and can affect the atmospheric oxidation capacity through

influencing the regional level of tropospheric hydroxyl radicals (OH) and the lifetime of methane (Peñuelas and Staudt 2010). Therefore, changes in isoprene emissions could modulate atmospheric composition and chemistry. An accurate estimate of isoprene emissions is important for air quality and climate change studies, and thus warrants in-depth investigation.

Many previous studies have shown that biogenic isoprene emissions are not only dependent on changes in environmental factors, such as canopy temperature, light, soil moisture etc., but also related to changes in vegetation type, vegetation distribution, leaf area, and leaf age (Guenther et al. 2006). Some recent studies have reported that changes in atmospheric CO_2 concentration might

promote or limit isoprene emissions from vegetation. Increasing CO₂ concentration could enhance vegetation productivity (Piao et al. 2011), and hence indirectly promote isoprene emissions. However, it is unclear whether a raised atmospheric CO₂ concentration would increase isoprene emissions intrinsically (Peñuelas and Staudt 2010). Several laboratory and field studies have indicated that the isoprene emissions rate has an inverse relationship in response to rising CO₂ concentration in the short and long term because an elevated CO₂ concentration might uncouple isoprene emissions from photosynthesis and suppress isoprene emissions at leaf level (Rosenstiel et al. 2003; Possell, Hewitt, and Beerling 2005) (known as 'the CO₃-inhibition effect').

A number of previous studies have attempted to introduce the CO₂-inhibition effect into chemical transport models for examining the impact of climate change on isoprene emissions, although the relationship between CO₂ and isoprene is not fully understood (Arneth et al. 2007; Heald et al. 2009; Wilkinson et al. 2009; Lathière, Hewitt, and Beerling 2010; Possell and Hewitt 2010). Arneth et al. (2007) found that observed leaf isoprene emissions were reproduced well by implementing the isoprene response to CO₂ concentration into the model used in their study, which is expressed as the ratio of the leaf internal CO₂ concentration at ambient $CO_2 = 370$ ppmv to the leaf internal CO₂ concentration. They also suggested the CO₂-inhibition effect could be large enough to counteract the increases in isoprene emissions due to CO₂-induced enhancement of vegetation productivity and leaf area growth. According to the isoprene measurements taken from aspen trees growing under four different CO₂ concentrations, Wilkinson et al. (2009) proposed a sigmoidal, Hill-reaction type isoprene-CO₂ curve to describe the short-term and longterm isoprene response to changes in atmospheric CO₂. Heald et al. (2009) used a global coupled land-atmosphere model with the CO₂-isoprene parameterization of Wilkinson et al. (2009) to explore the potential role of CO₂ in isoprene emissions over 2000-2100. They suggested the projected increases in isoprene emissions due to the warming climate in 2100 could be significantly modified by including the CO₂ inhibition effect. Recently, Possell and Hewitt (2010) improved the isoprene-CO₂ response curve by considering a wide range of tree species from tropical to temperate regions. The aforementioned studies indicate the important impacts of changes in atmospheric CO₂ concentration on isoprene emissions simulation, but large discrepancies remain among these isoprene-CO₂ relationships and related parameters. Such differences can result in different isoprene emissions predictions. Recently, a number of studies have examined biogenic emissions in China (Li et al. 2012; Li, Chen, and Xie 2013; Fu and Liao 2014; Li and Xie 2014). However, those studies were mostly

focused on the estimation and spatiotemporal variation of biogenic VOC emissions, and investigating the roles of meteorological factors and vegetation parameters in biogenic emissions. No previous studies have quantified the impact of CO₂ concentration on isoprene emissions in China, or evaluated the uncertainty of the CO₂-inhibition effect.

In this study, we use a global chemical transport model (GEOS-Chem) to estimate the biogenic isoprene emissions in China over 2006–2011, and examine the effect of CO₂ inhibition on regional isoprene emissions. We quantify the CO₃-inhibition effect on the simulation of isoprene emissions and the uncertainty in comparison with different CO₂ inhibition parameterizations in the model, based on previous studies. We further discuss the implications for regional air quality due to the inclusion of CO₂ inhibition effects on isoprene emissions.

2. Model and methods

We use the GEOS-Chem global 3D chemical transport model, version 9-02 (http://acmg.seas.harvard.edu/geos/) to simulate the biogenic isoprene emissions in China over 2006–2011. The model is driven by the assimilated meteorological data from MERRA (http://gmao.gsfc.nasa.gov/ merra/), with a horizontal resolution of 2.0° latitude × 2.5° longitude and a reduced vertical resolution of 47 levels. A similar modelling framework was used by Fu and Tai (2015). In GEOS-Chem, biogenic isoprene emissions are calculated by the Model of Emissions of Gases and Aerosols from Nature (MEGAN v2.1) (Guenther et al. 2006, 2012), which is estimated as a function of plant functional type-specific emission factors (E_0 , μg C m⁻² h⁻¹) modulated by environmental activity factors (normalized ratio) to account for the effects of temperature (γ_T) , light (γ_D) , leaf age (γ_{age}) , LAI, soil moisture (γ_{sm}) and CO_2 concentration (γ_{CO_2}) . The biogenic isoprene emissions rate (E) in each model grid cell is computed as

$$E = E_0 \cdot \text{LAI} \cdot \gamma_T \cdot \gamma_p \cdot \gamma_{\text{age}} \cdot \gamma_{\text{sm}} \cdot \gamma_{\text{CO}_2}. \tag{1}$$

However, the default model does not consider the effect of soil moisture and CO_2 inhibition by setting $\gamma_{sm} = 1$ and $\gamma_{\rm CO_2}=$ 1. To account for the ${\rm CO_2}$ -inhibition effect, the empirical relationships between CO₂ concentration and the isoprene emissions rate from previous studies are applied in this work. For examining the impact of CO₂ inhibition on isoprene simulation, we perform four sets of simulations: [noCO₂_ctrl], [wCO₂_A], [wCO₂_W], and [wCO₂P]. For each set, a six-year simulation is performed with meteorological fields from 2006 to 2011, present-day vegetation parameters and fixed anthropogenic emissions at year-2005 levels (Streets et al. 2003; Zhang et al. 2009). The simulation [noCO₂_ctrl] is the control

simulation without the CO₂-inhibition effect. The simulations [wCO $_2$ A], [wCO $_2$ W], and [wCO $_2$ P] are the sensitivity simulations, which are similar to [noCO₂_ctrl] but with different CO₂-inhibition parameterizations. In the simulation [wCO₂_A], the empirical CO₂-isoprene relationship is from Arneth et al. (2007) (Equation (2)); and in the simulation [wCO₂_W], the CO₂ inhibition parameterization of Wilkinson et al. (2009) is used (Equation (3)). The simulation [wCO₂_P] applies the CO₂-inhibition effect given by Possell and Hewitt (2010) (Equation (4)). The CO₂ concentrations used for calculating the $\gamma_{\rm CO}$ in all the simulations are from the GEOS-Chem CO₂ simulation during the same period.

As shown in Arneth et al. (2007), the additional activity factor associated with the CO, suppressed effect can be modelled in Equation (2):

$$\gamma_{\text{CO}_2} = \frac{C_{i-370}}{C_i},\tag{2}$$

where C_i is the leaf internal CO_2 concentration, and C_{i-370} is the leaf internal concentration at ambient $CO_2 = 370 \text{ ppmv}$ (under non-water-stressed conditions). According to Possell, Hewitt, and Beerling (2005), C, is about 70% of the ambient CO_2 concentration (C_a) .

We also apply the isoprene-CO₂ relationship from Wilkinson et al. (2009), which is

$$\gamma_{\text{CO}_2} = I_{s_{\text{max}}} - \left[\frac{I_{s_{\text{max}}} \times (C_i)^h}{(C_*)^h + (C_i)^h} \right],$$
(3)

where I_s is the isoprene emissions rate, $I_{s_{max}}$ is the estimated asymptote at which further decreases in CO₂ concentration (C_i) would suppress isoprene emissions, and C_i and hare the Hill-type coefficients used to adjust the sigmoidal slope of the relationship between I_{ε} and C_{i} . In this study, the I_s , C_s , and h are determined from the measurements of plants grown at four different CO₂ concentrations (400, 600, 800, and 1200 ppmv), by best-fit lines. The parameters are obtained from Wilkinson et al. (2009, Table 1).

The third normalized ratio to account for the effect of CO₂ concentration is provided by Possell and Hewitt (2010),

$$\gamma_{\text{CO}_2} = a/(1 + a \times b \times C_a), \tag{4}$$

where $\gamma_{CO_2} = 1$ at a CO_2 concentration equal to 370 ppmv, and a and b are empirical coefficients. Here, we use the fitting parameters a = 8.9406 and b = 0.0024 ppm⁻¹, which are provided in Possell and Hewitt (2010, Figure 5).

3. Results

Without the CO₂ effect ([noCO₂_ctrl]), the simulated annual isoprene emissions rate averaged over 2006–2011 across China is about 12.62 Tg C yr⁻¹. The annual isoprene emissions rate simulated in this study is within the range of 9.3–23.4 Tg C yr⁻¹ reported for China (Fu and Liao 2012; Li, Chen, and Xie 2013). Isoprene emissions are highest in summer (June-July-August, JJA) and lowest in winter (December-January-February, DJF). The isoprene emissions in DJF, MAM (March-April-May), JJA, and SON (September-October-November) account for 4.8%, 18.5%, 55.0%, and 21.7% of the annual emissions, respectively (Table 1). Figure 1(a) shows the spatial distribution of summertime and annual mean isoprene emissions from the [noCO₂_ctrl] simulation averaged over 2006–2011. We find that, largely, isoprene emissions are simulated over southern (south of 35°N) and northeastern China in summer, which are within the range of 10–40 mg C m⁻² d⁻¹, and mostly attributable to the increases in temperature and vegetation density. In addition, the spatial distribution of isoprene emissions is generally consistent with the distribution of trees in China, as trees are considered the highest isoprene emitter, compared with other vegetation types such as crops and grass.

We find that the spatial patterns of CO₂ effects on isoprene emissions are similar over China, despite the amount of influence exhibiting some discrepancies among the three different CO₂-inhibition parameterizations (Figure 1(b–d)). As shown in Figure 1, the CO₂ effect can substantially reduce isoprene emissions in summer in most of eastern China, especially in the eastern regions of Sichuan Province and southeastern China. The strong reductions in isoprene emissions in those regions are primarily due to the atmospheric CO₂ concentrations in those regions being generally higher than in other regions. As reported

Table 1. Estimates of isoprene emission rates in China averaged over 2006–2011 (Tg C yr⁻¹). Also shown are the percentage changes of isoprene emissions (%) between the experiments with ([wCO2 A], [wCO2 P], and [wCO2 W]) and without ([noCO2-ctrl]) the CO₂-inhibition effect.

Isoprene	[noCO ₂ _ctrl]	Change (%)		
		[wCO ₂ _A] – [noCO ₂ _ctrl]	$[wCO_2P] - [noCO_2ctrl]$	$[wCO_2W] - [noCO_2ctrl]$
Annual	12.62	-7.4	-6.6	-2.7
Winter	0.60	-7.9	-7.1	-2.7
Spring	2.34	-8.3	-7.5	-2.7
Summer	6.93	-7.1	-6.3	-2.6
Autumn	2.75	-7.3	-6.6	-2.6

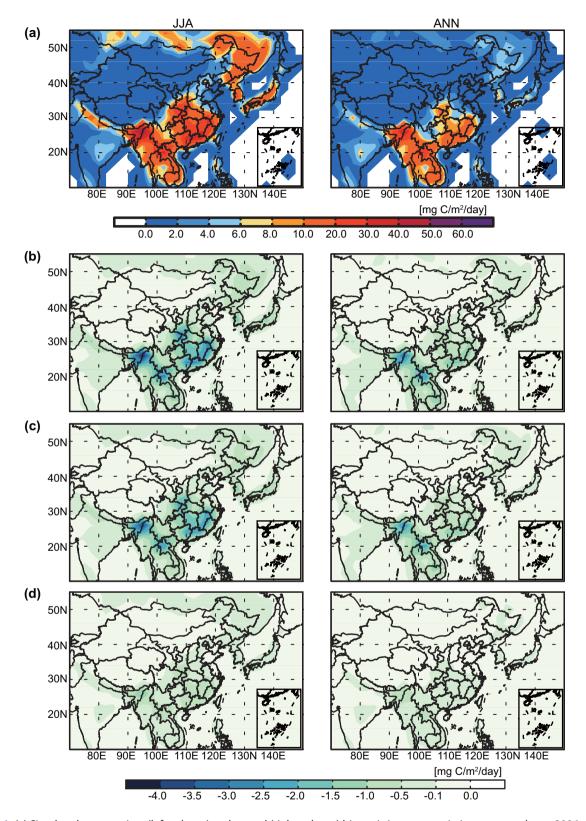


Figure 1. (a) Simulated summertime (left column) and annual (right column) biogenic isoprene emissions averaged over 2006–2011 in China in $[noCO_2_ctrl]$. (b) Spatial distribution of changes in isoprene emissions as a result of the CO_2 -inhibition effect using the scheme of Arneth et al. (2007) ($[wCO_2_A] - [noCO_2_ctrl]$). (c) As in (b) but with the scheme of Possell and Hewitt (2010) ($[wCO_2_P] - [noCO_2_ctrl]$). (d) As in (b) but with the scheme of Wilkinson et al. (2009) ($[wCO_2_W] - [noCO_2_ctrl]$).

by a number of laboratory-based studies, when CO_2 changes within the range of 200–1200 ppmv, trees grown

at lower CO₂ concentrations exhibit significantly higher isoprene emission rates compared with those grown at

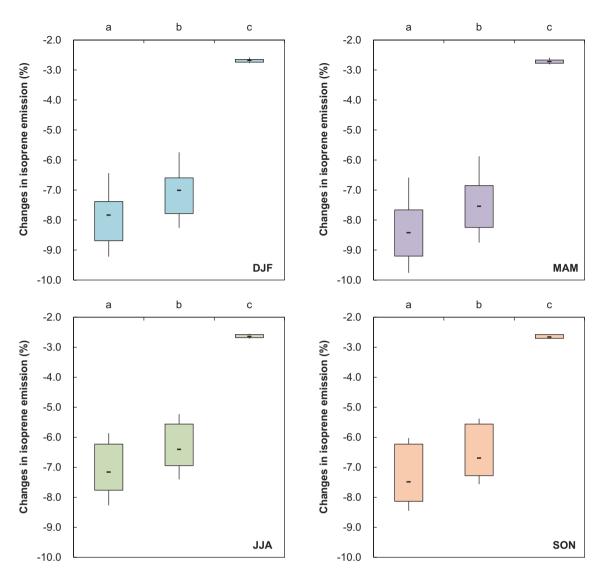


Figure 2. Box-plots for the annual variations of the CO_2 -inhibition effect on seasonal isoprene emissions in China from three different parameterizations of the isoprene– CO_2 relationship during the years 2006–2011.

Notes: 'a' represents the CO_2 effect on isoprene emissions estimated from ([wCO_2_A] – [noCO_2_ctrl]); 'b' represents the CO_2 effect estimated from ([wCO_2_P] – [noCO_2_ctrl]). For each parameterization, the bottom and top of the box are the first and third quartiles, and the band inside the box is the median within six years. The ends of the whiskers (lines extending vertically from the boxes) represent the maximum and minimum of the values over 2006–2011. The width of the box with whiskers can indicate the degree of variation in the data.

higher $\rm CO_2$ concentrations (Possell, Hewitt, and Beerling 2005; Wilkinson et al. 2009). The plant physiological and biochemical mechanisms responsible for the $\rm CO_2$ suppression of isoprene emissions are poorly understood, but likely relate to the changes in the substrates for isoprene biosynthesis and metabolism at leaf level under increased $\rm CO_2$ concentrations (Rosenstiel et al. 2003). In the eastern regions of Sichuan Province and parts of southeastern China, isoprene emissions decline by more than 9% to a maximum of -3.5 mg C m $^{-2}$ d $^{-1}$ in summer when the $\rm CO_2$ -inhibition effects are included, indicating the importance of the $\rm CO_2$ -inhibition effect on estimates of isoprene emissions. The consideration of $\rm CO_2$ inhibition reduces annual isoprene emissions by around 2.7%-7.4% (Table 1).

Figure 2 represents the effects of CO_2 inhibition on seasonal isoprene emissions over China during 2006–2011 from $[wCO_2_A] - [noCO_2_ctrl]$, $[wCO_2_P] - [noCO_2_ctrl]$, and $[wCO_2_W] - [noCO_2_ctrl]$. In all seasons, the maximum reduction in isoprene emissions due to the CO_2 effect is obtained in $[wCO_2_A]$, followed by $[wCO_2_P]$ and $[wCO_2_W]$. The CO_2 effect on isoprene emissions exhibits little seasonal variation in all sensitivity simulations. However, the changes in isoprene emissions resulting from CO_2 inhibition display interannual variation during 2006–2011, except those in $[wCO_2_W]$. In $[wCO_2_A]$, the isoprene emissions in DJF over China decrease by -7.8% (median value) when taking into account CO_2 inhibition, and the decline in isoprene emissions in MAM due to CO_2 inhibition varies from -9.8% to

-6.6%, with a median of -8.4%. In JJA and SON, the CO₂ effect leads to a decrease in isoprene emissions of -8.5% to -6.0% in [wCO₂_A] over 2006–2011. The reductions in isoprene emissions induced by the CO₂ effect in [wCO₂_P] are similar to the results of [wCO₂_A]. We also find that the interannual variation in isoprene emissions, induced by the effect of CO₂ inhibition, is quite important compared to the impact of land-cover and land-use change. As shown by Fu and Liao (2012), simulated isoprene emissions in summer over eastern China change by 5%–8% as a result of vegetation change alone over 2001–2006.

As shown above, estimates of isoprene emissions can differ depending on the CO₂-isoprene response curve, which also represents a major source of uncertainty in projecting future isoprene emissions as the atmospheric CO₂ concentration continues to rise. The discrepancies in the three CO₂-isoprene relationships likely result from the differences in quantitative algorithms and empirical coefficients, which are obtained from different plant species in growth-chamber experiments. For example, some studies describe the response as a purely mathematical relationship based on the experimental growth of two isoprene-emitting herbaceous species under different CO₂ levels (Possell, Hewitt, and Beerling 2005; Arneth et al. 2007). Whereas, Wilkinson et al. (2009) constructed an empirical relationship through consideration of the principles of enzyme kinetics based on the measured responses of temperate cottonwood and aspen trees under controlled-environment growth chambers. Possell and Hewitt (2010) attempted to define the CO₂-inhibition effect using laboratory measurements of tropical tree species (Acacia nigrescens). In order to better understand the calculated CO₂ inhibition in the model, we further quantify the CO₂-inhibition effect and its uncertainty according to the results of the sensitivity simulations. As shown in Figure 3, in the presence of CO₂-isoprene interaction, the annual present-day (2006–2011) isoprene emissions over China reduce by $5.6\% \pm 2.3\%$, while the isoprene emissions in DJF, MAM, JJA, and SON are cut by $5.9\% \pm 2.5\%$, $6.2\% \pm 2.7\%$, $5.3\% \pm 2.1\%$, and $5.5\% \pm 2.2\%$, respectively.

The significance of the variations induced by $\rm CO_2$ inhibition can also be demonstrated when compared with the changes in isoprene emissions resulting from climate change alone. For instance, without the $\rm CO_2$ effect, changes in meteorological conditions between the two three-year periods of 2006–2008 and 2009–2011 enhances summertime isoprene emissions by about 50 Gg C/month in China (1 Gg = $\rm 10^9$ g) (isoprene averaged over 2009–2011 minus isoprene averaged over 2006–2008). However, inclusion of the $\rm CO_2$ effect can partly offset such increases or even reverse the sign. The simulated summertime isoprene increment from the period 2006–2008 to the period 2009–2011 on average shrinks by 20% when the

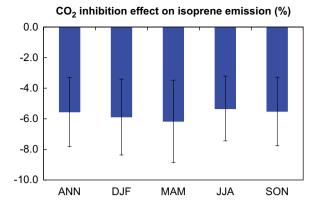


Figure 3. Estimates of the CO_2 -inhibition effect on isoprene emissions from existing parameterizations in the model. Note: Uncertainties in the CO_2 -inhibition effect on annual (ANN), winter (DJF), spring (MAM), summer (JJA), and autumn (SON) isoprene emissions due to the differences in the isoprene— CO_2 response curves are shown as the standard deviation.

CO₂ effect is considered in [wCO₂_W], while the CO₂ effect in [wCO $_{\gamma}$ A] and [wCO $_{\gamma}$ P] can completely nullify such an increase and lead to 70 Gg C/month and 60 Gg C/month reductions in isoprene emissions, respectively. The results in this study imply that the inclusion of CO₂ inhibition can substantially affect the sensitivity of isoprene emissions to changes in meteorological conditions. The impact of CO₂ inhibition can be more significant on multi-decadal scales than the magnitudes reported here. Recently, a few studies have indicated that the inclusion of CO₂ inhibition would generally reduce the sensitivity of air pollution to climate and vegetation change under future projection. Tai et al. (2013) reported that, over 2000–2050, the inclusion of CO₂ inhibition leads to reduced sensitivity of surface ozone and SOA (by more than 50%) to climate and natural vegetation change where isoprene emissions are important, implying a benefit of air quality in populated, high-NO, regions.

4. Discussion and conclusions

A global transport model (GEOS-Chem) is used in this study to simulate the isoprene emissions over China, with the inclusion of CO_2 -isoprene interaction, from 2006 to 2011. Without the CO_2 -inhibition effect, the simulated isoprene emissions rate is approximately 12.62 Tg C yr⁻¹ across China. To quantify the impact of CO_2 inhibition on isoprene emissions, three estimates of isoprene emissions with different parameterizations of the CO_2 -isoprene response are compared. The results indicate that the CO_2 -inhibition effect, which is not included in most chemistry or climate modelling studies, is significant in estimating isoprene emissions. For instance, applying the Wilkinson et al. (2009) scheme in [wCO $_2$ -W] decreases annual isoprene emissions by ~3% relative to the control simulation ([noCO $_2$ -ctrl])

without CO₂ inhibition. Whereas, applying the CO₂ inhibition scheme of Arneth et al. (2007) in [wCO₂_A] and Possell and Hewitt (2010) in [wCO₂P] reduces annual isoprene emissions by ~7% over China. This effect might be significant in regions where the CO₂ concentration and isoprene emissions are high. To summarize, the impact of CO₂ inhibition can lead to an annual isoprene emissions decrease of $5.6\% \pm 2.3\%$. Regionally, summertime isoprene emissions might be cut by more than 9% when the CO₂-inhibition effect is included. Compared with the changes in isoprene emissions resulting from climate change alone on the multi-decadal scale, the reductions in isoprene emissions induced by CO₂ inhibition are significant. Sensitivity studies have shown that, in China, changes in meteorological conditions between the late 1980s and mid-2000s led to increases in isoprene emissions by 17% (Fu and Liao 2014). The changes in isoprene emissions resulting from climate change can be modified if the CO₂ inhibition is accounted for in the model.

There are a few studies that have indicated that the CO₂-isoprene effect might have a potential influence for projected ozone air quality or SOA concentrations under future climate change scenarios (Young et al. 2009; Tai et al. 2013), because they are both sensitive to the spatial and temporal variations of biogenic isoprene emissions (Fu and Liao 2012). In this study, the inclusion of CO₂ inhibition may lead to a reduction in SOA concentrations (by ~10%) where isoprene emissions largely decrease. Future work should focus on a more systematic analysis of the variation of in ozone and SOA to CO₂-isoprene integration under climate change. However, the CO₂-isoprene response curves are built on a limited number of measurements for several species in earlier studies, so the parameterizations of CO₂-isoprene interaction still pose a challenge for accurate estimates of isoprene emissions in China at present. In addition, a few previous experimental studies pointed out that inhibition of the isoprene emissions rate occurs in the presence of an increased CO₂ concentration for both short-term exposure (seconds to minutes) and long-term exposure (weeks to months). The responses of isoprene emissions to changes in CO₂ concentration might be different on various time scales. For instance, the response of isoprene emissions might be driven by adjustments in existing metabolic components during a single day. Whereas, on time scales at which leaves develop and grow (weeks or months), the response of isoprene emissions is likely driven by the adjustments in gene expression and the production of new metabolic components (Wilkinson et al. 2009). Here, we only focus on the effects of CO₂ inhibition on monthly and seasonal isoprene emissions, rather than diurnal isoprene emissions, mostly because the changes in sub-ambient CO₂ concentration (intercellular CO₂) over shorter time scales are scarce. The short-term effect of CO₂ inhibition on daily isoprene emissions is still a challenge and full of large uncertainty, especially in China. Wilkinson et al. (2009) reported that the sensitivity of the isoprene emissions rate to intercellular CO₂ could decrease with long-term exposure to increased atmospheric CO, if the intercellular CO₂ concentration changes between 200 and 400 ppmv. Since the diurnal variation of isoprene emissions is strong, the diurnal effect of CO₂ concentration on isoprene emissions definitely warrants further investigation. More specific information on, and measurements of, extensive and representative plant species from major isoprenerelease regions are required to improve CO2-isoprene parameterization in future studies in China.

Acknowledgements

The MERRA data used in this study were provided by the Global Modeling and Assimilation Office (GMAO) at the NASA Goddard Space Flight Center through the NASA GES DISC online archive.

Funding

This work was supported by the National Natural Science Foundation of China [grant number 41405138]; the National High Technology Research and Development Program of China [grant number 2013AA122002].

References

Arneth, A., R. K. Monson, G. Schurgers, U. Niinemets, and P. I. Palmer. 2008. "Why Are Estimates of Global Terrestrial Isoprene Emissions So Similar (and Why is This Not So for Monoterpenes)?" Atmospheric Chemistry and Physics 8: 4605-4620. doi:http://dx.doi.org/10.5194/acp-8-4605-2008.

Arneth, A., Ü. Niinemets, S. Pressley, J. Bäck, P. Hari, T. Karl, S. Noe, et al. 2007. "Process-Based Estimates of Terrestrial Ecosystem Isoprene Emissions: Incorporating the Effects of a Direct CO₂-Isoprene Interaction." Atmospheric Chemistry and Physics 7: 31-53. doi:http://dx.doi.org/10.5194/acp-7-31-2007.

Fiore, A. M., V. Naik, D. V. Spracklen, A. Steiner, N. Unger, M. Prather, D. Bergmann, et al. 2012. "Global Air Quality and Climate." Chemical Society Reviews 41: 6663-6683. doi:http:// dx.doi.org/10.1039/C2CS35095E.

Fu, Y., and H. Liao. 2012. "Simulation of the Interannual Variations of Biogenic Emissions of Volatile Organic Compounds in China: Impacts on Tropospheric Ozone and Secondary Organic Aerosol." Atmospheric Environment 59: 170–185. doi:http://dx.doi.org/10.1016/j.atmosenv.2012.05.053.

Fu, Y., and H. Liao. 2014. "Impacts of Land Use and Land Cover Changes on Biogenic Emissions of Volatile Organic Compounds in China from the Late 1980s to the mid-2000s: Implications for Tropospheric Ozone and Secondary Organic Aerosol." Tellus B 66: 24987. doi:http://dx.doi.org/10.3402/ tellusb.v66.24987.

Fu, Y., and A. P. K. Tai. 2015. "Impact of Climate and Land Cover Changes on Tropospheric Ozone Air Quality and Public Health in East Asia between 1980 and 2010." Atmospheric Chemistry and Physics 15: 10093-10106. doi:http://dx.doi. org/10.5194/acp-15-10093-2015.



- Guenther, A. B., X. Jiang, C. L. Heald, T. Sakulyanontvittaya, T. Duhl, L. K. Emmons, and X. Wang. 2012. "The Model of Emissions of Gases and Aerosols from Nature Version 2.1 (MEGAN2.1): An Extended and Updated Framework for Modeling Biogenic Emissions." *Geoscientific Model Development* 5: 1471–1492. doi:http://dx.doi.org/10.5194/gmd-5-1471-2012.
- Guenther, A., T. Karl, P. Harley, C. Wiedinmyer, P. I. Palmer, and C. Geron. 2006. "Estimates of Global Terrestrial Isoprene Emissions Using MEGAN (Model of Emissions of Gases and Aerosols from Nature)." *Atmospheric Chemistry and Physics* 6: 3181–3210. doi:http://dx.doi.org/10.5194/acp-6-3181-2006.
- Heald, C. L., M. J. Wilkinson, R. K. Monson, C. A. Alo, G. Wang, and A. Guenther. 2009. "Response of Isoprene Emission to Ambient CO₂ Changes and Implications for Global Budgets." Global Change Biology 15: 1127–1140. doi:http://dx.doi.org/10.1111/j.1365-2486.2008.01802.x.
- Lathière, J., C. N. Hewitt, and D. J. Beerling. 2010. "Sensitivity of Isoprene Emissions from the Terrestrial Biosphere to 20th Century Changes in Atmospheric CO₂ Concentration, Climate, and Land Use." *Global Biogeochemical Cycles* 24: GB1004. doi:http://dx.doi.org/10.1029/2009gb003548.
- Li, L. Y., Y. Chen, and S. D. Xie. 2013. "Spatio-Temporal Variation of Biogenic Volatile Organic Compounds Emissions in China." *Environmental Pollution* 182: 157–168. doi:http://dx.doi.org/10.1016/j.envpol.2013.06.042.
- Li, M., X. Huang, J. Li, and Y. Song. 2012. "Estimation of Biogenic Volatile Organic Compound (BVOC) Emissions from the Terrestrial Ecosystem in China Using Real-Time Remote Sensing Data." Atmospheric Chemistry and Physics Discussion 12: 6551–6592. doi:http://dx.doi.org/10.5194/acpd-12-6551-2012.
- Li, L. Y., and S. D. Xie. 2014. "Historical Variations of Biogenic Volatile Organic Compound Emission Inventories in China, 1981–2003." *Atmospheric Environment* 95: 185–196. doi:http://dx.doi.org/10.1016/j.atmosenv.2014.06.033.
- Peñuelas, J., and M. Staudt. 2010. "BVOCs and Global Change." *Trends in Plant Science* 15: 133–144. doi:http://dx.doi.org/10.1016/i.tplants.2009.12.005.
- Piao, S., P. Ciais, M. Lomas, C. Beer, H. Liu, J. Fang, P. Friedlingstein, et al. 2011. "Contribution of Climate Change and Rising CO₂ to Terrestrial Carbon Balance in East Asia:

- A Multi-Model Analysis." *Global and Planetary Change* 75: 133–142. doi:http://dx.doi.org/10.1016/j.gloplacha.2010.10.014.
- Possell, M., and C. N. Hewitt. 2010. "Isoprene Emissions from Plants Are Mediated by Atmospheric CO₂ Concentrations." *Global Change Biology* 17: 1595–1610. doi:http://dx.doi.org/10.1111/j.1365-2486.2010.02306.x.
- Possell, M., C. N. Hewitt, and D. J. Beerling. 2005. "The Effects of Glacial Atmospheric CO₂ Concentrations and Climate on Isoprene Emissions by Vascular Plants." *Global Change Biology* 11: 60–69. doi:http://dx.doi.org/10.1111/j.1365-2486.2004.00889.x.
- Rosenstiel, T. N., M. J. Potosnak, K. L. Griffin, R. Fall, and R. K. Monson. 2003. "Increased CO₂ Uncouples Growth from Isoprene Emission in an Agriforest Ecosystem." *Nature* 421: 256–259. doi:http://dx.doi.org/10.1038/nature01312.
- Streets, D. G., T. C. Bond, G. R. Carmichael, S. D. Fernandes, Q. Fu, D. He, Z. Klimont, et al. 2003. "An Inventory of Gaseous and Primary Aerosol Emissions in Asia in the Year 2000." *Journal of Geophysical Research: Atmospheres* 108 (D21): 8809. doi: http://dx.doi.org/10.1029/2002jd003093.
- Tai, A. P. K., L. J. Mickley, C. L. Heald, and S. L. Wu. 2013. "Effect of CO₂ Inhibition on Biogenic Isoprene Emission: Implications for Air Quality under 2000 to 2050 Changes in Climate, Vegetation, and Land Use." *Geophysical Research Letters* 40: 3479–3483. doi:http://dx.doi.org/10.1002/Grl.50650.
- Wilkinson, M. J., R. K. Monson, N. Trahan, S. Lee, E. Brown, R. B. Jackson, H. W. Polley, P. A. Fay, and R. A. Y. Fall. 2009. "Leaf Isoprene Emission Rate as a Function of Atmospheric CO₂ Concentration." *Global Change Biology* 15: 1189–1200. doi:http://dx.doi.org/10.1111/j.1365-2486.2008.01803.x.
- Young, P. J., A. Arneth, G. Schurgers, G. Zeng, and J. A. Pyle. 2009. "The CO₂ Inhibition of Terrestrial Isoprene Emission Significantly Affects Future Ozone Projections." *Atmospheric Chemistry and Physics* 9: 2793–2803. doi:http://dx.doi.org/10.5194/acp-9-2793-2009.
- Zhang, Q., D. G. Streets, G. R. Carmichael, K. B. He, H. Huo, A. Kannari, Z. Klimont, et al. 2009. "Asian Emissions in 2006 for the NASA INTEX-B Mission." *Atmospheric Chemistry and Physics* 9: 5131–5153. doi:http://dx.doi.org/10.5194/acp-9-5131-2009.