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## Estimation of the isoprene emission from the Inner Mongolia grassland

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### ABSTRACT

Measurements of isoprene emissions, solar spectral radiation, temperature and relative humidity were carried out at a grassland site in the Inner Mongolia, China during the growing seasons in 2002 and 2003. Isoprene emissions are dependent on PAR (Photosynthetically Active Radiation) and temperature nonlinearly. PAR controls the main processes related to isoprene emission, thus, PAR energy balance is used to establish quantitative relationship between isoprene emission and its affecting factors. An empirical Equation of isoprene emission was built on the basis of PAR energy balance. The calculated values were in good agreement with those measured for 2002 and 2003 summer seasons, the relative biases of 70% estimated emissions were within 50% compared to measured fluxes. The chamber changes the inside environment and emission fluxes, the emission differences were estimated by using the empirical Equation. The results show that isoprene emission flux around the noon decreases by 37% when the chamber is used, i.e., the biggest effect was resulted from PAR difference caused by the chamber. Isoprene emission measured by chamber should be corrected. The empirical model of isoprene emission showed that isoprene emission fluxes were close to zero, when PAR was low in early morning and in late evening. Total isoprene emissions emitted from the grassland in the Inner Mongolia were 1.10 and 1.00 gC m<sup>-2</sup> during the growing seasons of 2002 and 2003, respectively, which contributed to about 3.1–4.3% and 2.8–3.9% to grass respiration. The averaged isoprene emission normalized to a standard light (1 500 μmol m<sup>-2</sup> s<sup>-1</sup>) and temperature (30 °C) condition was 482.8 μg m<sup>-2</sup> h<sup>-1</sup>.

**Keywords:** Grassland, isoprene, PAR energy balance, air temperature, water vapor pressure



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### 1. Introduction

Isoprene is the single largest source of biogenic volatile organic compounds (BVOCs) for the atmosphere in many areas (Guenther et al., 1995; Sharkey et al., 1999; Geron et al., 2002), its oxidation influences OH and ozone concentrations, and has a significant role in CO production, the formation of organic acids, the photochemical conversion of NO<sub>y</sub> species, and secondary organic aerosols (Guenther et al., 1999; Boge et al., 2006). Over 90% of isoprene emission is from vegetation (Guenther et al., 1995), the annual global isoprene emission ranges from about 500 to 750 Tg (440 to 660 Tg carbon) (Guenther et al., 2006). The importance of isoprene is further amplified by its high reactivity with the hydroxyl radical, O<sub>3</sub>, NO<sub>x</sub> (Geron et al., 2002; Pacifico et al., 2009; Taraborelli et al., 2009), and the photooxidation of isoprene is a substantial source of secondary organic aerosol (SOA) (Claeys et al., 2004a; Claeys et al., 2004b; Boge et al., 2006). The heterogeneous reaction of isoprene on acidic particles could be an important source of humic-like substances, which contribute 20 to 50% of the water-soluble organic aerosol (Limbeck et al., 2003). Isoprene and other BVOCs (Kleindienst et al., 1999) can be photooxidized to SOA. The positive and negative feedback between climate change and BVOCs emission is another important issue and should be investigated (Pacifico et al., 2009). Many BVOC emission algorithms and models are developed and applied to estimate isoprene and monoterpene emissions (Tingey et al., 1980; Guenther et al., 1991; Guenther et al., 1993; Guenther et al., 1995; Niinemets et al., 1999; Martin et al., 2000; Zimmer et al., 2000; Zimmer et al., 2003; Guenther et al., 2006; Arneth et al., 2007; Pacifico et al., 2011), which are based on known controlling factors and their processes. BVOC emissions are associated with many

factors, including the two key factors, PAR, temperature, and other factors, humidity, water and drought, O<sub>3</sub>, CO<sub>2</sub>, UV/UVB, leaf area index, plant functional type, etc. (Guenther et al., 2006; Pacifico et al., 2009; Penuelas and Staudt, 2010). The physical, chemical and photochemical processes related to above parameters are interactive, therefore, accurate estimation of BVOC emission is still a challenge. Isoprene emission models should take into account of not only PAR and temperature, but also other factors mentioned above. The more important is that they should consider the interactions between isoprene and atmospheric substances [including gases, liquids and particles (GLPs)], and PAR energy. Therefore, energy method is another way to study this complicated photochemical system, interactions between isoprene emission, PAR and atmospheric substances in a realistic atmosphere. The emission models based on energy methods are more objective and practical to simulate isoprene emissions for natural atmospheric conditions than for laboratory controlled conditions. In addition, there are still unmeasured BVOCs and their photochemical oxidation products (SOA) (Di Carlo et al., 2004; Karl et al., 2009; Kim et al., 2009) and associated photochemical processes in the atmosphere (Bai, 2009; Bai, 2011), energy method has another advantage that we can pay our main attention on grasping isoprene and its variation, its key energy role in the atmosphere. We do not need focus on studying every reaction of isoprene with atmospheric substances, which is impossible to understand all reactions associated with isoprene and GLPs (e.g., SOA) in the atmosphere at present. To improve our understanding of regional and global isoprene emissions, more measurement and model studies are needed. Temperate semi-arid grassland of China is an important ecosystem in the Northern Hemisphere, isoprene emission from the Inner Mongolia Grassland has a special charac-

teristic. The aim of this paper is to fully investigate the relationship between isoprene emission and its affecting factors, i.e., PAR energy dynamic balance associated with BVOC emissions and their interactions with the atmospheric substances, so as to understand isoprene emission in the Inner Mongolia grassland.

## 2. Instrumentations, Sampling and Analysis

The investigation site [aneurolepidium chinense sample plot (ACSP)] was a fenced permanent area (400 m×600 m) containing a mixture of typical grasses, which was located at the Inner Mongolia Grassland Ecosystem Research Station, Chinese Academy of Sciences (43°26′~44°08′N, 116°04′~117°05′E) in the Baiyinxile Pasture. Common species at this site mainly include *Aneurolepidium chinense*, *Carex duriuscula*, *Stipa grandis*, *Agropyron cristatum*, etc. (Bai et al., 2006). The hottest month is July with the average temperature of 18.8 °C, and the annual precipitation is 350 mm. There is chestnut and dark chestnut soil in grassland correlating to typical steppe and meadow-steppe respectively (Jiang, 1985).

Emissions were measured using a static enclosure technique (Bai et al., 2006). In short, a square stainless steel base (0.9 m×0.9 m×0.15 m) was inserted into the ground, and a square transparent polycarbonate chamber (0.3 m height) was placed on the base. Air samples were pumped in 4 Liter passivated stainless steel canisters to 2 atmospheres. A background air sample was collected before covering the chamber, and the second sample was collected about 30 minutes after covering the chamber. The canisters had been previously cleaned and were vacuumed before use. Samples of 2002 summer were analyzed in the laboratory in the Beijing by gas chromatograph with a flame ionization detector (GC-FID) (Bai et al., 2003; Bai et al., 2006). Samples of 2003 summer were analyzed in the laboratories at the South Dakota School of Mines and Technology and NCAR (USA), the analysis technique was described by Greenberg et al. (1999). Solar radiation, including solar global radiation  $Q$ , scattering radiation  $S$ , direct radiation  $D$ , PAR, was measured by a solar radiation system (Bai et al., 2006).

In the summer season of 2002, 45 samples were collected, i.e. 5 samples were collected each day at 2 hours interval, and 3 days for each month, June (26<sup>th</sup>, 27<sup>th</sup>, and 28<sup>th</sup>), August (13<sup>th</sup>, 15<sup>th</sup>, 16<sup>th</sup>, and 31<sup>st</sup>) and September (2<sup>nd</sup>, 3<sup>rd</sup>). The averaged ratio of isoprene concentration to total VOC concentration was 82% for the 2002 summer season.

## 3. Results and Discussions

The emission flux  $E$  ( $\mu\text{gC m}^{-2} \text{h}^{-1}$ ) of isoprene was calculated by the equation:

$$E = h \Delta C / \Delta t \quad (1)$$

where,  $h$  is the net height of the chamber (m),  $\Delta t$  is the time the grass was covered by the chamber (hour),  $\Delta C$  is the difference of isoprene concentrations during the enclosure period  $\Delta t$  ( $\mu\text{gC m}^{-3}$ ).

Daytime emission fluxes of isoprene showed obvious diurnal, daily and seasonal variations, and its influencing factors PAR and air temperature (outside the chamber) also showed similar variation patterns. It was found that emission fluxes of isoprene were also affected by the clouds, especially for the daily variation of every month, which is the indirect effect from clouds to PAR, then to isoprene emission. Figures 1 and 2 show the variations of isoprene emission and cloudiness, PAR and air temperature (outside the chamber) in 2002, respectively.

Based on analyzing observational data (45 group data), isoprene emission flux ( $E$ ) was strongly correlated with PAR (outside the chamber) with correlation coefficient ( $R$ ) of 0.86.  $E$  was also strongly correlated with both inside temperature ( $T$ ) and inside WVP (water vapor pressure,  $e$ , hPa) with  $R$  values of 0.82 and 0.79, respectively. The lower  $R$  values were found between  $E$  and both outside  $T$  and outside WVP with 0.48 and 0.46, respectively. So, PAR,  $T$  (leaf temperature) and WVP (inside the chamber) are important factors influencing  $E$  for its diurnal, daily and seasonal variations.

## 4. The Relationship between Isoprene Emission Flux and Its Factors

Considering the attenuation of PAR by the chamber, the measurements of PAR inside and outside the chamber were carried out during 2002 summer. The relationship between the transmissivity ( $R_T$ , %) of the chamber and the solar zenith angle ( $Z$ ) was determined based on observational data, a good agreement was obtained with correlation coefficient ( $R$ ) of 0.991, and the equation is:

$$R_T = 73.2 \cos Z + 9.4 \quad (2)$$

Then, PAR inside the chamber can be calculated by the measurements of PAR outside the chamber.

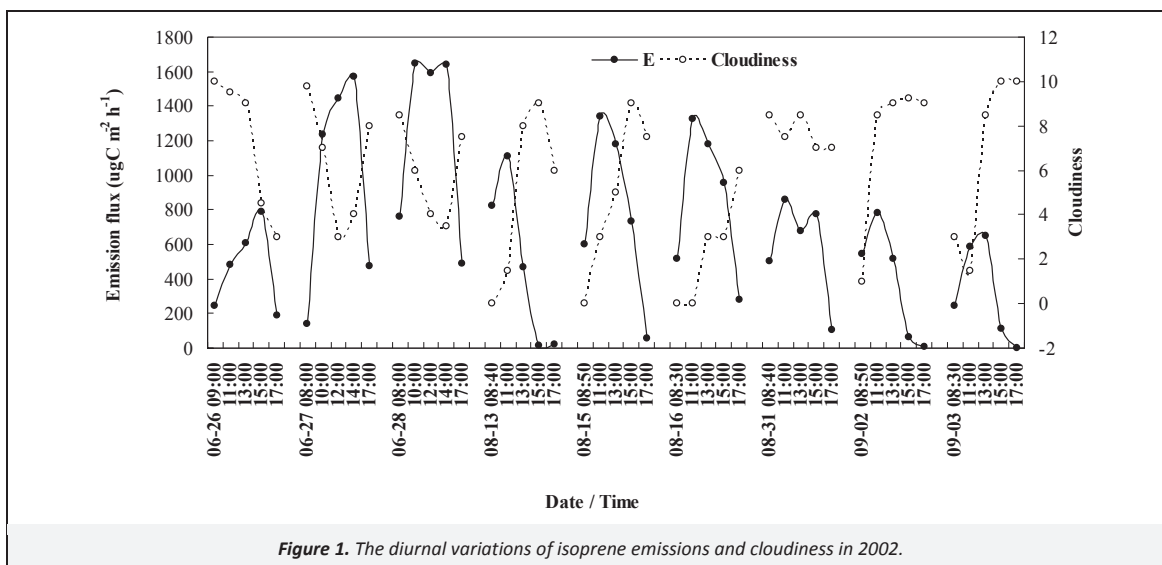


Figure 1. The diurnal variations of isoprene emissions and cloudiness in 2002.

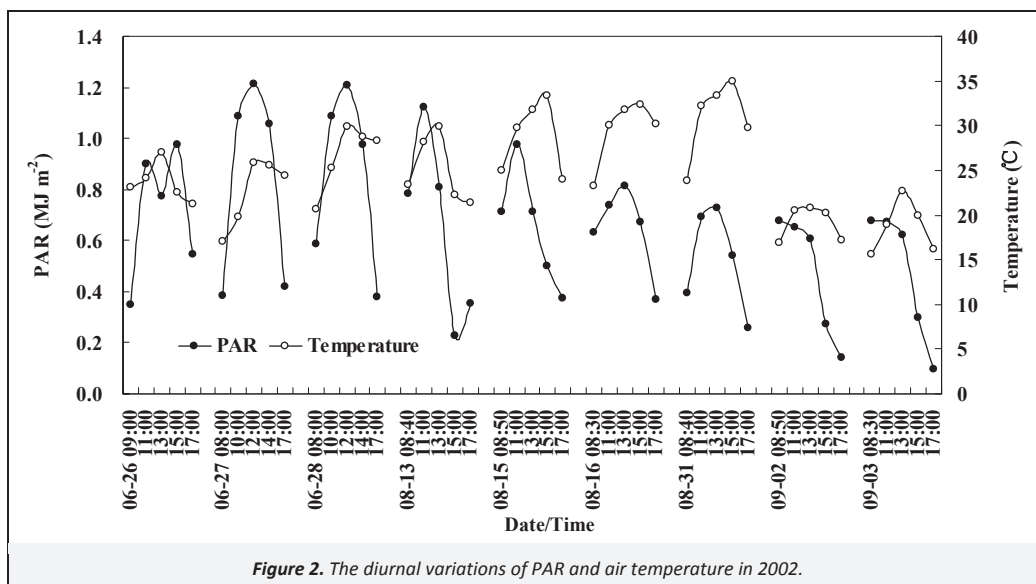


Figure 2. The diurnal variations of PAR and air temperature in 2002.

Because PAR and temperature are recognized as two important controlling factors in isoprene emissions, they were selected in the simple simulation of  $E$  for the first step. The quantitative relationship between logarithm of  $E$  and PAR,  $T$  inside the chamber was determined by statistical analysis, based on 45 data in 2002 summer:

$$\ln E = 0.40 \text{ PAR} + 0.15 T - 0.30 \quad (3)$$

PAR and  $T$  were the sums of PAR and temperature averages during the covering time, their  $R$  was 0.91.

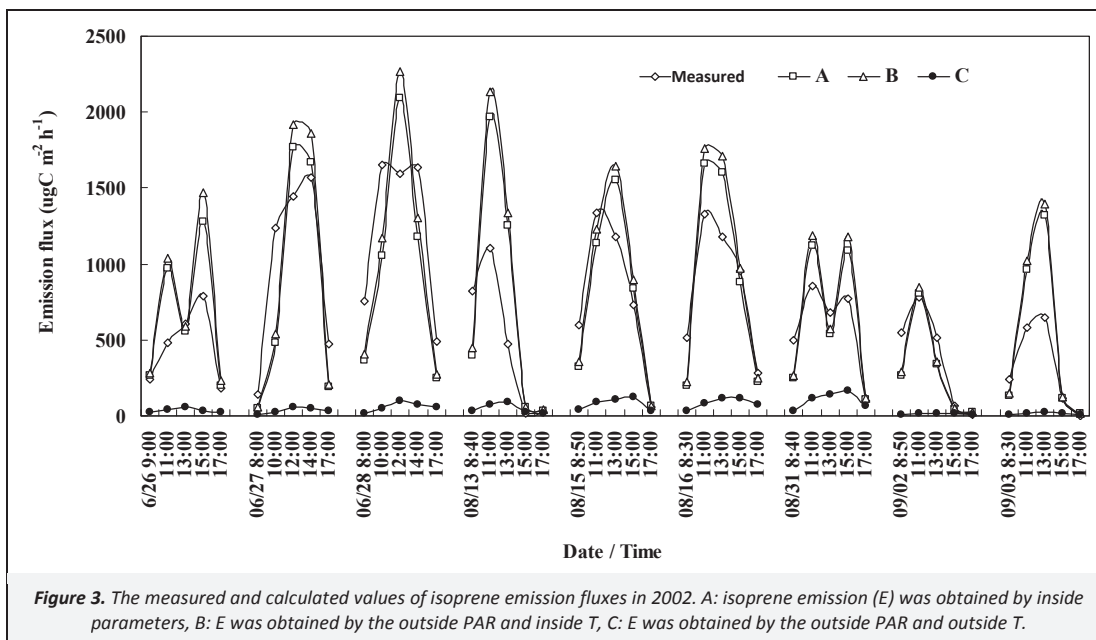
Using Equation (3),  $E$  inside the chamber was calculated and expressed by  $A$ . For the differences of PAR,  $T$  and  $E$  between inside and outside the chamber, it is necessary to calculate  $E$  in natural atmospheric conditions. Then, two conditions were considered: (1) modification of only solar radiation (i.e. PAR), i.e.,  $E$  was obtained by the outside PAR and inside  $T$ , and expressed by  $B$ , (2) modification of solar radiation and temperature, i.e.,  $E$  was obtained by the outside PAR and outside  $T$ , and expressed by  $C$ .

Figure 3 shows the observed and calculated isoprene emissions at three conditions in 2002. The calculated values of  $A$  agreed well with those measured for diurnal, daily and seasonal variations. The calculated values of  $B$  were a little higher than that of  $A$ . During the measurements of PAR transmissivity in 2002 summer, PAR transmissivity varied from 65.4% to 83.2%. Because PAR outside the chamber is higher than the inside, the estimated isoprene emission  $B$  was higher than  $A$ . The calculated values of  $C$ , the actual emission fluxes in natural atmospheric conditions were much lower than that of  $B$  and  $A$ , which was unreasonable. Isoprene emission should not be dependent on correlation equation only, and be calculated on the basis of physical and chemical mechanisms.

Solar radiation is an energy source for the growth of plants. The plants absorb or utilize PAR, and then take part in physiological activities with the exchange of gases, water and energy between inside and outside the plants, or between plants and the atmosphere. Then, PAR transmission and utilization may be used to study isoprene emissions. When PAR transfers in the atmosphere, it is absorbed, scattered and utilized by the substances (in gas, liquid and particle phases), including (1) PAR attenuation by isoprene, which is called isoprene factor and expressed by  $e^{-k_1 E t m}$ . Isoprene can react with OH radicals,  $O_3$ ,  $NO_x$ , and can be photooxidized to SOA. During these processes, PAR energy would be consumed/utilized by isoprene. It is assumed the attenuation of

isoprene to PAR obeys the Lambert-Beer's law. This expression is developed from the  $NO$ ,  $NO_2$  expression in  $O_3$ -OH radical photochemistry in UV wavelength band (Bai, 2010a),  $k_1$  is attenuation coefficient of isoprene and assumed to be equal to 1.  $t$  is time of the chamber covering,  $m$  the air mass in the mid-time of covering period. (2) PAR energy absorption and or utilization by GLPs through OH radicals when they are taking part in chemical and photochemical (C&P) reactions in the atmosphere, which is called photochemical factor and expressed as  $e^{-k_2 W m}$ , which is the development of energy utilization by GLPs in chemical and photochemical reactions from UV to PAR wavelength band (Bai, 2009; Bai, 2010a; Bai, 2013). OH radical production mechanisms in the visible region has been reported by Li et al. (2008) (by electronically excited  $NO_2^*$  reaction with water molecules) and Matthews et al. (2005). The  $e^{-k_2 W m}$  term can represent this energy role (Bai, 2010b). (3) The scattering roles by all substances, and the multi-scattering and reflecting between all substances and the surface and vegetation, which is called scattering factor and expressed as  $e^{-S/Q}$ ,  $S$  and  $Q$  are solar scattering radiation and solar global radiation.  $S/Q$  can represent the scattering roles of GLP objectively, and is easily obtained at meteorological observation stations. Isoprene and the other VOCs are highly reactive, and can react with  $O_3$ , OH radicals,  $NO_x$  (Geron et al., 2002; Pacifico et al., 2009). During the photooxidation of isoprene and the other VOCs (through OH radicals), the SOA can be formed (Kleindienst et al., 1999; Limbeck et al., 2003; Claeys et al., 2004a; Claeys et al., 2004b; Boge et al., 2006), and the chemical and photochemical reactions between the gas-liquid-particle is ongoing, then, PAR (also UV) energy is transferred, consumed (and scattered) by all substances in the atmosphere. So, the above three terms are used to describe the different energy roles and processes, respectively.

It is well known that PAR and temperature are the main controlling factors of isoprene emission, and their roles are considered and expressed in the isoprene equation. The parameter of water vapor pressure was considered in photochemical term ( $e^{-k_2 W m}$ ), water vapor has a close relationship with the temperature and relative humidity.  $W$  is the water vapor content in the whole atmospheric column. Water vapor, temperature and humidity are interacted, and any changes in the temperature would result in the change of water vapor and humidity. The water vapor is another controlling factor for isoprene emission (Bai et al., 2003; Section 3, this study), and should be considered in the model. One objective of this study is to investigate key processes of isoprene emission by using an energy method to analyze field observational data and quantify energy relationships in the atmosphere, so as to get a reliable energy relationship.



Solar energy or PAR is the energy source for the grass growth and its all activities, including the processes of isoprene emission. Leaf temperature, water vapor in the grass, soil and atmosphere are mainly controlled by solar energy. Though it is unavoidable to disturb the natural conditions between inside and outside the chamber, and results in significant differences on PAR, leaf temperature, water vapor pressure, PAR is the main energy source to control biological activities of the grasses. PAR balance method can simplify all processes associated with isoprene emission, which are complicated and inter-reacted. It is essence to capture main energy processes controlling isoprene emissions in natural conditions.

It is well known that the substances in the atmosphere absorb solar ultraviolet radiation and visible radiation (400–700 nm), which is called actinic radiation. But, it is difficult to calculate direct and indirect actinic absorption directly, because the limitation of our knowledge about all C&P reactions, which include homogeneous and heterogeneous processes.

The important role of photochemical term and how to estimate it are introduced here briefly. When solar UV radiation transfers through the atmosphere and reaches the ground, it is influenced by 3 factors: (1) ozone absorption, which is called ozone term and expressed as  $e^{-k_1 O_3 m}$ , here  $k_1 = (3.30 \pm 0.07) \times 10^5 \text{ (Pa cm)}^{-1}$  (Gushin, 1963),  $O_3$  is the column total ozone amount in unit atm-cm,  $m$  is the air mass. (2) Photochemical term, which was expressed as  $e^{-k_2 W m}$  and obtained by empirical method as follows. Considering the fact that the ratio of UV to solar global radiation ( $Q_{uv}/Q$ ) arriving on the ground is basically a constant, about  $5.5\% \pm 0.4\%$  for 8 stations over China (Zhou, 1986), and a similar conclusion of our Beijing observations (Bai and Wang, 1993). So, there is a hypothesis that  $Q_{uv}'/Q' = C'$ , where  $Q_{uv}'$  is UV energy absorption by all substances in C&P reactions,  $Q'$  is solar shortwave ( $\lambda = 0.70\text{--}2.845 \mu\text{m}$ ) absorption by water vapor,  $C'$  is a coefficient. The absorption of water vapor to solar shortwave radiation is expressed as  $\Delta S = 0.172 \text{ (mW)}^{0.303}$ ,  $m$  is air mass,  $W$  is the water vapor content in the whole atmospheric column and was calculated from empirical equation using water vapor pressure ( $e$ , hPa) at ground level,  $W = 0.21e$ . If only water vapor is considered and the atmosphere is plane-parallel, the solar radiation at the horizontal surface:

$$I_s = I_0 \cos Z - \Delta S = I_0 e^{-k_2 W m} \cos Z \quad (4)$$

then,

$$e^{-k_2 W m} = 1 - \Delta S / (I_0 \cos Z) \quad (5)$$

Here,  $I_0 = 1367 \text{ W m}^{-2}$ . The coefficient  $C'$  is determined based on the statistical analysis of field observational data. (3) Scattering term and was expressed as  $e^{-S/D}$ ,  $S$  and  $D$  are the solar scattering radiation and solar direct radiation. Then the UV radiation at the ground  $Q_{uv}$  is equal to the summation of above three terms. Based on the statistical analysis on monthly mean observational data of Beijing ( $39^\circ 46' \text{N}$ ,  $116^\circ 58' \text{E}$ ) in 1990 (Bai and Wang, 1995), the following equation was determined:

$$Q_{uv} = C_1 e^{-k_1 O_3 m} + C_2 e^{-k_2 W m} + C_3 e^{-S/D} + C_0 \quad (6)$$

Here, all parameters of solar radiations were monthly mean daily sums,  $W$  was the monthly average, and  $m$  was the value at noon on the 15<sup>th</sup> each month.  $C_1$ ,  $C_2$ ,  $C_3$  and  $C_0$  were coefficients and constant and determined by the statistical analysis. In clear sky conditions (cloudiness  $N < 3/10$ ) and all sky conditions ( $N$  is from 0 to 10/10), three conditions are considered (Bai, 2009): (1) only ozone term, (2) ozone and photochemical terms, (3) three terms. The calculated results  $Q_{uv}$ ,  $R$  value between  $Q_{uv}$  and different factors and the standard errors ( $\sigma$ ) are given by Bai (2009). The calculated results agreed well with the observed, especially for conditions 2 and 3. The maximum and averaged relative biases were decreased evidently when photochemical term was added in UV calculation under clear and all sky conditions, indicating photochemical term (i.e. total UV energy absorption by all substances in the atmosphere) plays very important roles and can represent the total UV energy absorption by all substances. Using the point of view of energy, empirical method was used to estimate energy absorptions by all substances.

Then, PAR energy absorption by all substances was estimated in PAR band by applying this similar method in UV band.  $D = Q_{PAR}'/Q'$  ( $Q_{PAR}'$  was PAR energy absorption by all substances in C&P reactions), which was also determined by the analysis of experimental data.

So, PAR energy relationship at the ground ( $Q_{PAR}$ ) can be determined as follows by using the natural laboratory (Bai and Baker, 2004a):

$$Q_{PAR} = D_1 e^{-k1Et/m} + D_2 e^{-k2wm} + D_3 e^{-S/D} + D_0 \quad (7)$$

The meaning of isoprene factor  $e^{-k1Et/m}$  should be discussed here.  $e^{-k1Et/m}$  was taken out from photochemical term  $D_2 e^{-k2wm}$ , which is the direct PAR absorptions and indirect PAR consumption by all substances except isoprene. Then, isoprene term  $D_1 e^{-k1Et/m}$  is PAR utilization (or PAR attenuation) during the C&P reactions, when isoprene reacts with OH radical,  $O_3$ ,  $NO_x$ , other VOCs, etc. It is the application from the study of ozone-NO-NO<sub>2</sub>-OH radical photochemical system in UV band to ozone-isoprene-OH radical photochemical system in PAR or visible band (Bai, 2010a).

Considering the shape of the chamber, PAR downward was much larger than the horizontal in the chamber, PAR attenuation in vertical direction was mainly considered and  $e^{-k1Et/m}$  was changed to  $e^{-k1Et/m}$ . Based on the statistical analysis of data ( $n=45$ ), an empirical equation was determined:

$$e^{-k1Et/m} = -0.12 Q_{PAR} + 0.07 e^{-k2wm} - 0.003 e^{-S/D} + 0.96 \quad (8)$$

Here, all parameters of solar radiation were sums during the covering period,  $m$  was the air mass at the mid-time of covering period, and  $W$  and  $e$  were averages during the covering time. The results showed that PAR was highly correlated with its three factors [in the Equation (7)], and its  $R$  was 0.94. The Equation (8) was used to calculate isoprene emission flux easily. The statistical analysis showed that the isoprene term was also highly correlated with its three affecting factors, its  $R$  was 0.91.

The emission flux of isoprene (inside the chamber) were calculated by using Equation (8), and denoted as  $A$ .  $E$  differs between the inside and the outside of the chamber, then, modification of  $E$  was also made for two conditions: (1) Modification of solar radiation and denoted as  $B$ , i.e.,  $E$  was obtained by the outside PAR,  $S$ ,  $Q$ , inside water vapor content. (2) Modification of solar radiation and water vapor content and remarked as  $C$ . i.e.,  $E$  was obtained by all parameters outside the chamber. For modification of solar radiation,  $S$  and  $Q$  were presumed the same attenuation rate by the chamber. The modification of temperature can be reflected in the modification of water vapor content. Now,

all isoprene estimations at three conditions and measured values are shown in Figure 4.

The calculated values of  $A$  agreed well with the measured for diurnal isoprene emissions. The absolute relative biases are shown in Table 1.

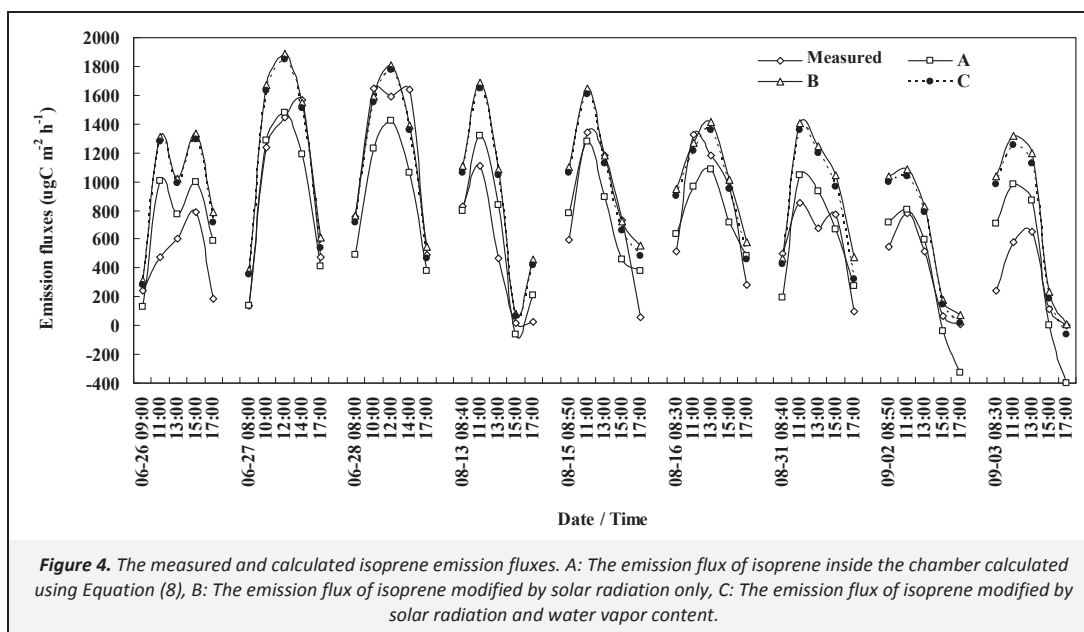
**Table 1.** The absolute relative biases ( $\delta$ ) between calculated values of  $A$  and measured values

$\delta$	>100%	100%~50%	50%~20%	<20%
Number	10	6	17	12
Ratio (%)	22.2	13.3	37.8	26.7

The relative biases of 65% estimated emissions were within 50% of measured fluxes. Temperature or leaf temperature is another important factor affecting isoprene emission and is mainly controlled by solar radiation energy. The correlation coefficient between PAR inside the chamber and leaf temperature during 2002 growing season was 0.80 at a confidence level 0.001. i.e., PAR energy is the key energy source for all kinds of activities of the grass.

Comparing the calculated values of  $A$  with that measured, it is found that the more the cloudiness, the bigger the relative biases. During the covering period and daytime in the summer season of 2002, the clouds including cloud type, height and cloudiness changed quickly, thus, how to quantitatively express the influences of clouds to solar radiation and then isoprene emission fluxes is still an important issue for future studies.

The calculated values of  $B$  were 21~57% (average, 37%) bigger than that of  $A$  around the noon, which is reasonable, because solar radiation was higher outside than inside. The calculated values of  $C$  were 2~9% (its average was 4%) smaller than that of  $B$  around the noon, because the water vapor content, temperature, and humidity were lower outside than that inside. The calculated values of  $C$  were 21~44% (its average was 29%) bigger than that of  $A$  around the noon. In fact, the calculated values of  $C$  are actual emission fluxes in natural atmosphere. Comparing calculated values  $A$ ,  $B$  and  $C$ , it can be found that bigger difference was caused by the difference of solar radiation, which indicates that it is necessary to modify solar radiation, and PAR is the first important factor controlling isoprene emission processes (Guenther et al., 1991; Guenther et al., 1995; Guenther et al., 2006).





For testing the reliability and applicability of this empirical equation, previous 25 of 45 data were selected to do the similar statistical analysis as above, the coefficients and constants were determined. The posterior 20 emission fluxes were calculated by new coefficients and constants. The results show that most estimated values agreed well with the measured, and the relative biases of 40% estimated emissions were within 50% of measured fluxes. Therefore, PAR energy balance can be used to deal with the main processes of isoprene emissions. Niinemets et al. (1999) also built a model of isoprene emission based on energetic requirements for isoprene synthesis and leaf photosynthetic property, and obtained good fits to diurnal courses of field measurements of isoprene emissions. So, the point of view of energy may be another approach to simulate isoprene emissions, and study the energy relationship between isoprene and its associated processes in the atmosphere.

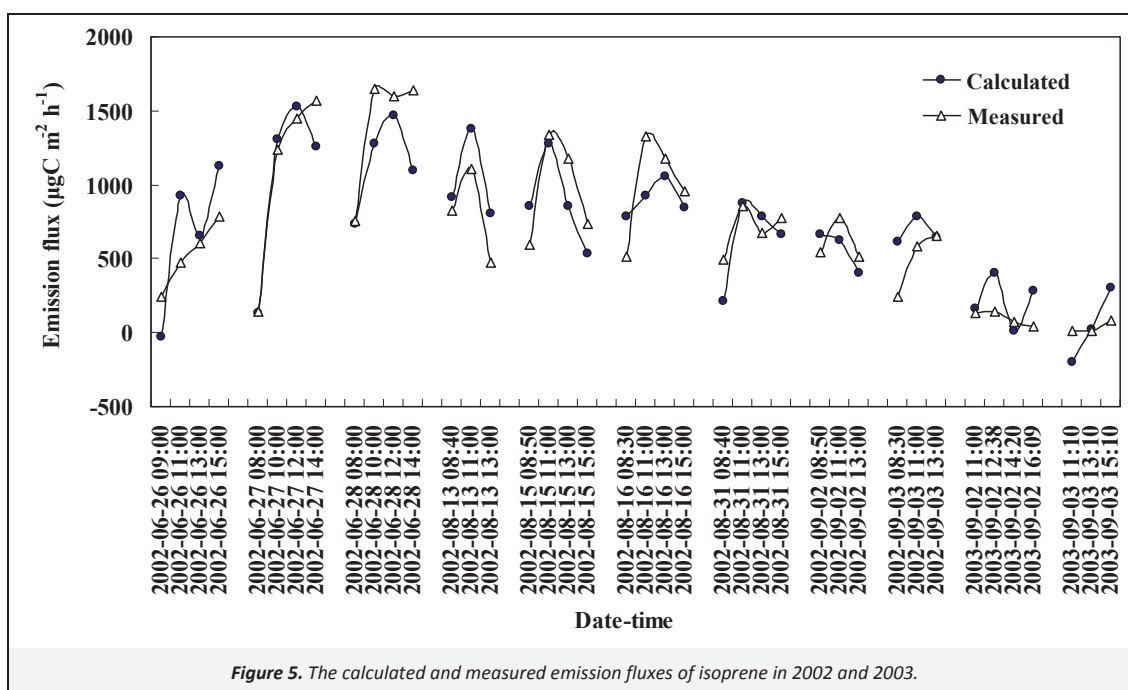
It is found that emission fluxes were close to zero at 17:00 on September 2<sup>nd</sup> and 3<sup>rd</sup>, August 13<sup>th</sup>, which was mainly caused by quick decrease of PAR, and corresponding decrease of water vapor content and temperature. In addition, almost all isoprene emissions (inside the chamber) at 8:00 and 17:00 during the summer of 2002 were close to or below zero by using this empirical equation, when PAR inside the chamber was less than 0.18 MJ m<sup>-2</sup>, and the other parameters kept their original levels, which indicated the empirical equation can capture isoprene diurnal variation well. Similarly, VOCs emissions from pasture in Australia were seldom detectable below 20 °C, and no emissions were observed after dark (Kirstine et al., 1998). So, the emissions before sunrise and after sunset were not measured during 2002 summer.

On September 2<sup>nd</sup> and 4<sup>th</sup>, 2003, two-day experiments were carried out at the same fixed ACSP plot, with 5 cartridge samples each day and total 10 samples were collected.

The study of isoprene emission at Xishuangbanna Tropical Botanic Garden (XTBG) in the middle of July 2002 showed that a similar empirical Equation for isoprene to (8) well-described

isoprene emissions on the basis of PAR energy balance, good agreement was also obtained. Under clear sky conditions, 111 half-hour emission fluxes of isoprene were obtained by fast isoprene system (FIS) in the rubber trees, the relative biases of 65% estimated emissions were within 50% of measured fluxes. To decrease the experimental errors of all measured parameters and explore the interaction and mutual-relationship between emission flux of isoprene and its affecting factors, the criterion for all parameters was selected, including PAR was 1 177–1 600  $\mu\text{mol m}^{-2} \text{s}^{-1}$ , emission flux of isoprene was 0.9–1.1  $\text{mgC m}^{-2} \text{h}^{-1}$ , air temperature was 21–24 °C, relative humidity was 65–80%, relative scattering factor was 0.1–0.4, which means the scattering role of clouds was less. Thus, 10 data was selected and used for the re-analysis as before. Newly estimated isoprene emissions were also in good agreement with the observed, and 57% of estimated emissions were within 50% of measured fluxes (Bai and Baker, 2004b). In fact, under relative good experimental conditions for all parameters, the energy quantitative relationships between all parameters are close to real and objective description of the law of nature.

In view of this, 55 measurements during the summer seasons of 2002 and 2003 were selected for the re-analysis. Then, the data for PAR less than 0.20 MJ m<sup>-2</sup> were eliminated, 40 data were kept including 7 data for 2003. Re-analyzing these data, a similar Equation to (6) and new coefficients were obtained. The calculated values of A also agreed well with measured, the relative biases for >100%, 100–50%, 50–20%, <20% were 17.5%, 12.5%, 32.5%, 37.5%, respectively, and the relative biases of 70% estimated emissions were within 50% of measured fluxes. Newly calculated results were a little improved, which implies that under the better atmospheric conditions, the improved quantitative relationship can be determined. 4 out of 7 data of relative biases bigger than 100% were cloudiness 9/10, 10/10, which was caused by the attenuation of clouds to PAR and then to isoprene emissions. In addition, isoprene emissions were smaller when cloudiness was higher. All above factors resulted in bigger relative biases. The isoprene empirical model can simulate diurnal, "seasonal" and "inter-annual" variations (Figure 5).



Using new coefficients and Equation (8), isoprene emission fluxes during the growing seasons of 2002 and 2003 were estimated. The growing season was from 10<sup>th</sup> May to 15<sup>th</sup> September each year. The input observational data were hourly sums for solar radiation and hourly averages for the other parameters. When hourly PAR was less than 0.34 MJ m<sup>-2</sup>, isoprene emissions were negative, similar to those measured at a tropical rain forest by Karl et al. (2004), thus they were set to zero. Daytime was selected from 8:00 to 18:00. Leaf temperature was assumed to be equal to air temperature, though there is a little difference. The calculated total emission fluxes of isoprene were 1.10 and 1.00 gC m<sup>-2</sup> during the growing seasons of 2002 and 2003, respectively, and their hourly maximum values were 2.33 and 1.93 mgC m<sup>-2</sup> h<sup>-1</sup>. The emission flux of isoprene was decreased 9.0% from 2002 to 2003 growing season, which was caused by synchronous decreases of PAR by 9.3% and temperature by 11.8%; the increase of water vapor pressure at the ground by 0.6%. Results showed that the averaged respiration of above ground grass in Inner Mongolia grassland during the growing season ranges from 95 to 130 mg CO<sub>2</sub> m<sup>-2</sup> h<sup>-1</sup> (daytime), making up 25% of grassland community respiration (Wang et al., 2004). Thus, isoprene emission emitted from the grass during the growing seasons of 2002 and 2003 contributed to about 3.1–4.3% and 2.8–3.9% to grass respiration (Bai and Baker, 2005). Considering the large area of grassland in China, it should be paid more attention to total isoprene and other BVOC emissions, it is not only in the potential influences of ozone and SOA photochemical formation, but also in the total carbon emission. The empirical relationship was built based on limited measurements, energy method or PAR energy dynamic balance associated with BVOC emissions and their interactions with the atmospheric substances is deserved to be studied and more validations are needed.

According to the estimation of isoprene emission calculated by the isoprene empirical model, monthly isoprene emission varied with the season evidently, higher in July, and lower in September, higher in 2002 and lower in 2003, which was mainly associated with PAR variation pattern, then temperature variation pattern (Figure 6). It means that PAR is a basic and key controlling factor, not only at half hour and hourly scales, but also at monthly and yearly scales.

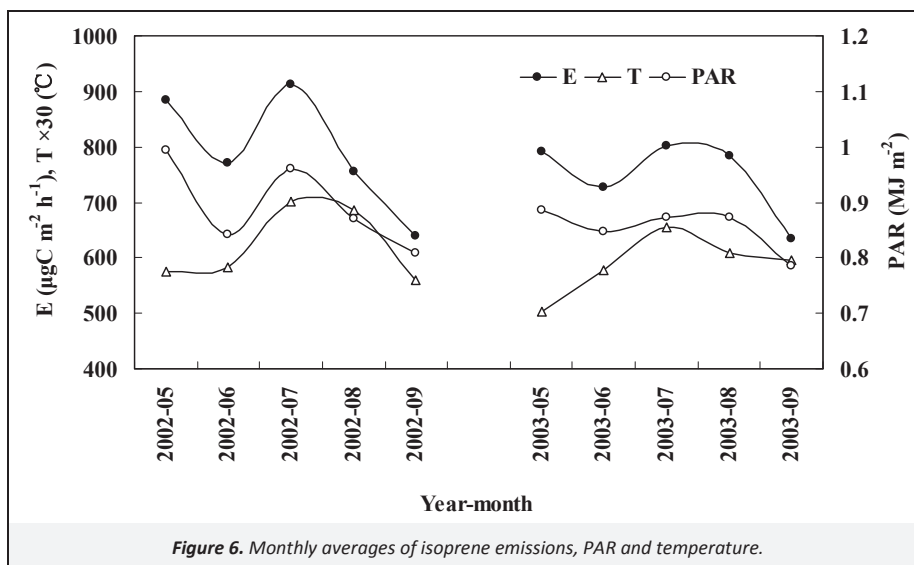
Isoprene emission model can be considered as an application of ozone empirical model (Bai, 2010a), from UV absorber to no UV and PAR absorption. The common characteristic is to study highly reactive gases, ozone and isoprene and their energy roles in the atmosphere. To investigate the energy roles between UV and

ozone, other factors at Dinghu Mountain forest, UV and isoprene, and other factors at the Inner Mongolia grassland, previous observational data (Bai, 2010a and the present study) were reanalyzed and new energy balance equations were determined, respectively (Bai, 2014):

$$Q_{UV}=F_1 e^{-k_1 E t / m} + F_2 e^{-k_2 w m} + F_3 e^{-S/Q} + F_0 \quad (9)$$

$$Q_{UV}=G_1 e^{-k_3 n_3 m} + G_2 e^{-k_4 n_4 m} + G_3 e^{-k_5 n_5 m} + G_4 e^{-k_6 w m} + G_5 e^{-S/Q} + G_0 \quad (10)$$

Here,  $F_1$ ,  $F_2$ ,  $F_3$ ,  $F_0$  were  $-0.36$ ,  $0.47$ ,  $0.10$  and  $0.01$ , for isoprene, photochemical and scattering terms at Inner Mongolia grassland, respectively.  $R^2=0.835$ , significance level=0.001. Data number for the analysis was  $n=28$ . The average of absolute relative bias between calculated and measured UV was 13.5%.  $G_1$ ,  $G_2$ ,  $G_3$ ,  $G_4$ ,  $G_5$  and  $G_0$  were  $0.26$ ,  $-0.05$ ,  $0.15$ ,  $0.73$ ,  $-0.06$  and  $-0.72$  for O<sub>3</sub>, NO (nitrogen oxide), NO<sub>2</sub> (nitrogen dioxide), photochemical, scattering terms at Dinghu Mountain forest, respectively.  $R^2=0.575$ , significance level=0.001,  $n=113$ . The average of absolute relative bias between calculated and measured UV was 16.2%. UV empirical models can simulate UV at these two ecosystems for about half hour and one hour UV values. Reanalyzing the isoprene emission flux measured above a rubber tree plantation at Xishuangbanna Tropical Botanic Garden (XTBG) (Bai and Baker, 2004b), a good relationship was found between PAR and isoprene, photochemical and scattering terms with  $R^2=0.712$  (significance level=0.001,  $n=169$ ), the coefficients were  $-2.9 \times 10^{-4}$ ,  $0.0012$ ,  $0.1425$  and  $0.9338$ , respectively (Bai, 2014). A new phenomenon was found, i.e., negative energy relationships were existed between UV and isoprene term at grassland and between UV and NO term at Dinghu Mountain forest, between PAR and isoprene term at XTBG, i.e., between no UV absorption gases and UV, and between no PAR absorption gases and PAR, which reveals UV and PAR energy consumption by isoprene and NO when they are taking part in chemical and photochemical reactions through OH radicals (Bai, 2009; Bai, 2011). It proves and improves our understanding of the indirect UV and PAR utilization by no UV and PAR absorbers in previous studies by Bai (2009; 2011). So, energy method can benefit us not only to capture variation characteristics of gases, the most important, to understand energy roles of GLPs, and energy utilization and transferring. The "energy flow" from the sun to all atmospheric substances deserves to be studied in the future at different sites.



Based on isoprene emission model, isoprene emission normalized to standard above-canopy light ( $1\ 500\ \mu\text{mol m}^{-2}\ \text{s}^{-1}$ ) and standard temperature ( $30\ ^\circ\text{C}$ ) conditions (Guenther et al., 2006) can be estimated. The PAR inside the chamber was calculated by Equation (2). Water vapor inside the chamber was calculated by the relationship between water vapor and temperature and relative humidity inside the chamber, and temperature  $30\ ^\circ\text{C}$  and original relative humidity. The original scattering factor was used so as to keep the same atmospheric conditions. Finally, the normalized isoprene emission for June and August, 2002 was  $482.8\ \mu\text{g m}^{-2}\ \text{h}^{-1}$  (in average), ranged from 413.6 to  $539.4\ \mu\text{g m}^{-2}\ \text{h}^{-1}$ . It is close to  $500\ \mu\text{g m}^{-2}\ \text{h}^{-1}$  calculated by algorithms of Guenther et al. (2006), which means the emission model is capable to capture key parameters of isoprene emissions.

## 5. Conclusions

During 2002 and 2003 summer, isoprene emissions and other parameters, PAR, temperature and relative humidity were measured in the Inner Mongolia grassland. PAR is the driving energy source for the activities of the grass, temperature can be considered as an indicator of dynamic balance of energy between the grass, soil, and atmosphere. The method of PAR energy balance is reasonable than "pure correlation" between isoprene emission and PAR and leaf temperature. An empirical equation for isoprene emissions was built, estimated isoprene emission fluxes were basically consistent with those measured, and the relative biases of 70% estimated emissions were within 50% of measured fluxes. The differences in isoprene emissions caused by the chamber should be corrected, especially the attenuation of PAR. The averaged bias for isoprene emission flux around the noon caused by the difference of PAR was 37%, which was much bigger than that of 4% caused by the difference of water vapor content. The isoprene empirical equation can capture isoprene diurnal variation. When PAR decreased to about  $0.18\ \text{MJ m}^{-2}$  and the other parameters kept their original levels in the early morning and in the late afternoon, isoprene emissions were close to zero, which means there is a PAR limiting or it is the main controlling factor. Integrating over the growing seasons of 2002 and 2003, the equivalent of 2.8%–4.3% of the carbon fixed by the grass was released to the atmosphere as isoprene. Area averaged isoprene emission normalized to a standard above-canopy light and temperature condition was  $482.8\ \mu\text{g m}^{-2}\ \text{h}^{-1}$ . Energy method can help us not only to better understand variations of the reactive gases, but also UV and PAR energy transferring and utilization in the atmosphere, and energy relationships between UV and PAR, and atmospheric substances.

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