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Estimation of the isoprene emission from the Inner Mongolia grassland

Jianhui Bai

LAGEO, Institute of Atmospheric Physics, Chinese Academy of Sciences, 100029, Beijing, China

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^{-2} 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^{-2} s^{-1}) and temperature (30 °C) condition was 482.8 µg m^{-2} h^{-1}.

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

Corresponding Author:
Jianhui Bai
☎ : *+86-10-82995079*
🖷 : *+86-10-82995073*
✉ : *bjh@mail.iap.ac.cn*
jianhuib@sina.com

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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_Y 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_3, NO_X (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_3, CO_2, 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 (26th, 27th, and 28th), August (13th, 15th, 16th, and 31st) and September (2nd, 3rd). 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 (μgC m^{-2} 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), Δt is the time the grass was covered by the chamber (hour), ΔC is the difference of isoprene concentrations during the enclosure period Δt (μgC 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.

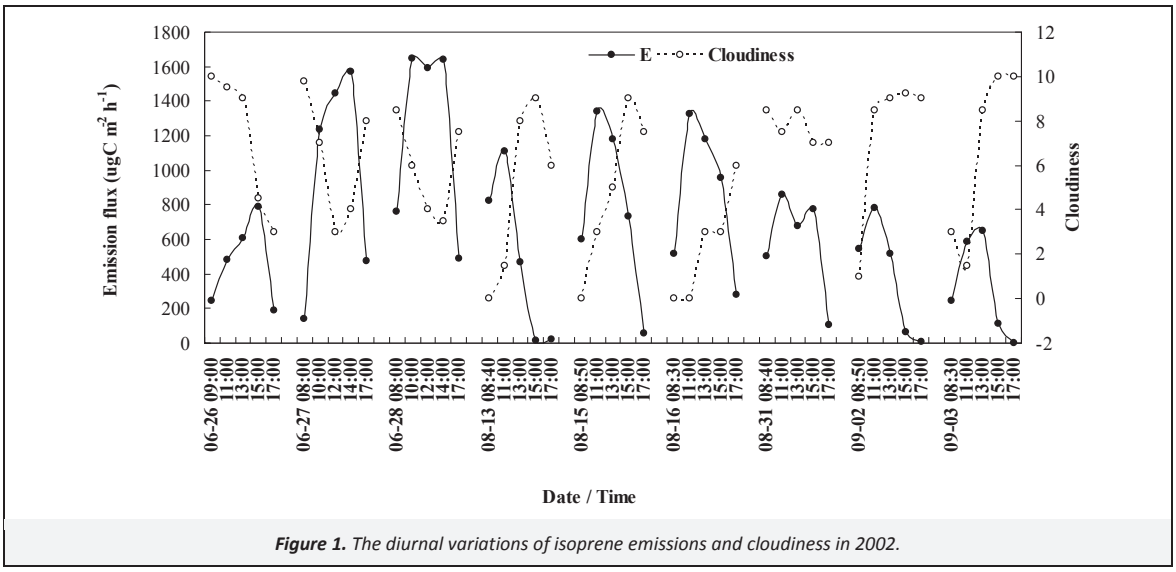

Figure 1. *The diurnal variations of isoprene emissions and cloudiness in 2002.*