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Isoprene and monoterpene emissions from an Inner Mongolia grassland

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Abstract

Terpenoid emissions were measured at a grassland site in Inner Mongolia, China during four campaigns over a 2-year period. Emissions were strongly correlated with light and temperature and the variations could be simulated using a canopy emission model. Substantial seasonal and interannual variations in isoprene emissions were also observed. Area averaged isoprene emissions normalized to standard above-canopy temperature and light conditions (30 °C and 1500 μmol $m^{-2} s^{-1}$) ranged from about 50 to 500 μg $m^{-2} h^{-1}$. These rates are more than an order of magnitude higher than those previously reported for temperate grasslands but are lower than emission rates observed from ground cover vegetation at higher latitudes. Isoprene emissions from this Inner Mongolia grassland may be dominated by emissions from sedges, e.g. *Carex appendiculata*. Total monoterpene emissions normalized to a standard temperature of 30 °C were only about 3 μg $m^{-2} h^{-1}$ and consisted primarily of carene and limonene with smaller contributions of α-pinene and β-pinene. A model sensitivity study showed that grass and other herbaceous ground cover can contribute >10% of the total isoprene emission from certain regions, such as Inner Mongolia, but are <4% on a global annual scale.

Keywords: Biogenic emissions inventory; Carex; China; Volatile organic compounds (VOCs)

1. Introduction

The chemical composition of the atmosphere is an important component of the global environment and observed trends in trace gas concentrations demonstrate that it is changing rapidly (Brasseur et al., 1999). Vegetation produces over 90% of the global annual nonmethane volatile organic compound (VOC) emissions which are dominated by the terpenoid compound, isoprene (Guenther et al., 1995). Isoprene oxidation influences OH and ozone concentrations and has a significant role in CO production, the formation of organic acids, and the photochemical conversion of NO_y species (Guenther et al., 1999).

Studies of biogenic VOC (BVOC) have focused on forests which are thought to be the dominant global source of BVOC. Although grasslands and pastures cover one quarter of the Earth's land surface (Guenther et al., 1995), relatively few studies

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have been conducted to determine the characteristics of BVOC emissions from these ecosystems (Fukui and Dosky 1998; Kirstine et al., 1998). Temperate semi-arid grassland covers about 35% of China and is an important ecosystem in the Northern Hemisphere. A preliminary sensitivity analysis of the uncertainties associated with BVOC emissions from China suggested that a lack of emission observations from grasslands could be a significant component of the total uncertainty. This paper describes field observations of isoprene and monoterpene emissions from a grassland in the Inner Mongolia region of China and discusses the implications for regional emission modeling.

2. Site Description and Methods

The site of the investigation was the Inner Mongolia Grassland Ecosystem Research Station (43°26′–44°08′N, 116°04′–117°05′E, 1200 m), which is operated by the Chinese Academy of Sciences in the Baiyinxile pasture. This grassland region has chestnut and dark chestnut soil corresponding to typical steppe and meadow-steppe, respectively (Jiang, 1985). The study region includes grazed and ungrazed areas containing a mixture of typical grasses, sedges and forbs. Common plant species in the study region include *Aneurolepidium chinense*, *Carex duriuscula*, *Stipa grandis*, *Agropyron cristatum*, *Serratula centauroides*, *Koeleria cristata*, *Cleistogenes squarrosa*, *Artemisia frigida*, *Allium senescens*, *Potentilla bifurca*, *Allium tenuissimum*, *Chenopodium album*, and *Dontostemon micranthus*. The dominant species in sampling plots are *A. chinense*, *Achnatherum sibiricum*, *S. grandis*, *Carex appendiculata*, *K. cristata*, *C. squarrosa*, *A. senescens*, and *A. tenuissimum*. The region has a cold and dry winter and a warm and wet summer resulting in a strong annual growth cycle that peaks in summer. The annual average temperature is −0.4 °C, July is the warmest month with an average temperature of 18.8 °C; the annual precipitation is 350 mm, 80% of which occurs from June to September.

A static enclosure method was used by inserting a square stainless steel base of 90 cm × 90 cm × 15 cm (height) into the ground to a depth of about 10 cm; a square transparent polycarbonate chamber of 90 cm × 90 cm × 30 cm (height) was then placed on the base during measurements. Two small electric fans were installed on opposite inner walls to mix the air in the chamber. The base was inserted into the ground at least 1 week before the initial sampling and remained there for the whole sampling period. A background air sample was collected immediately prior to covering the base with the chamber. A second sample was collected after about 30–40 min. The enclosure was removed between sampling intervals to dry the inner walls of the chamber and to allow the grass and the surface to return to ambient conditions. The emission flux E ($\mu g\,cm^{-2}\,h^{-1}$) of isoprene and monoterpenes was calculated as

$$E = h(DC/Dt), \quad (1)$$

where h is the height of the chamber (m), Dt is the sampling time (hour), and DC is the concentration difference during the enclosure period ($\mu g\,C\,m^{-3}$). The enclosure was closed only during the time of sampling.

Different sample collection and analytical methods were used during the 2002 and 2003 campaigns. Samples were collected into 4 L passivated (electropolished) stainless steel canisters for the three campaigns in 2002. The sampling pump was model PM 9659-022, KNF Neuberger, the sampling flow rate was about 2 L/min, and all tubing used in the experiment was Teflon. Canisters were cleaned prior to the experiment by purging with N_2 and were then evacuated. At the end of sample collection, the final canister pressure was about 2 atmospheres. Canisters were transported to the laboratory in Beijing and were analyzed within 1 week. Samples were quantified by gas chromatography (GC) with a flame ionization detector (FID) and identified by GC with a mass spectrometer (MS) (Varian Model 3400, Varian Inc., USA). The gas sample was introduced into a glass–lined stainless steel tube (10 cm × 0.53 mm i.d.) at −50 °C (for cryogenic preconcentration), and then thermally desorbed at 225 °C for about 2 min and transferred to the analytical column (60m × 0.32 mm, DB-1, J&W company, USA). The column oven temperature was held at 0 °C for 5 min, then was increased to 200 °C at 3 °C/min, and held for 5 min. Samples were calibrated using an *n*-pentane gas standard (10.5 ppm ± 2%, Scott Specialty Gases). The GC-MS was operated in total ion mode and the compounds from C_2 to C_{12} were analyzed. The precision of the GC-MS measurement is about ±10%. The samples for the September 2003 campaign were collected on solid absorbent cartridges. The samples were analyzed in laboratories at Rapid City (SDSMT) and Boulder (NCAR) USA

using GC-FID for quantification and GC-MS for identification using techniques described by Greenberg et al. (1994). The uncertainty associated with the 2003 campaign measurements is about 10%.

Solar global radiation, photosynthetically active radiation (PAR), and solar scattering radiation were measured during sampling periods with a model TBQ-4-1 solar radiation instrument (322 Institute of Jinzhou, China), the sensors for the spectral radiation were 270–3200 nm, 400–3200 nm, 700–3200 nm, respectively; their sensitivity and stability were 5–10 mV $kW^{-1}m^2$ and $\leqslant \pm 2\%$. The PAR was derived from the subtraction of two measurements of 400–3200 and 700–3200 nm. The collection and recording frequency of the solar spectral radiation was 1 Hz. PAR inside the chamber was calculated by the quantitative relationship between the transmissivity of chamber and solar zenith angle, and the measured PAR outside the chamber. In addition, temperature and humidity were measured inside and outside the chamber and averaged over 5 min intervals. The temperature inside the chamber was typically about 16 °C higher than ambient air. The relative humidity in the chamber was about 50% higher than ambient air. The temperature and humidity sensors inside the chamber were placed on the grass about 5 cm above the ground. An approximate estimate of cloudiness was also recorded every 5 min. Above ground biomass was determined by first cutting the vegetation at ground level and then drying at 75 °C until the mass was constant.

All measurements during 2002 were made on a single plot, referred to here as plot 1, in order to investigate diurnal and seasonal variations. The 2003 measurements were made at plot 1 and thirteen other plots to investigate spatial variations. The 2002 samples were collected on 3 days of each month from June to September (26, 27, 28 June, 13, 15, 16 August, 31 August, 2, 3 September). All samples were collected on days with no precipitation. Five samples were collected on each day at 2 h intervals. A total of 45 canisters was collected during the summer of 2002 and analyzed for isoprene. Thirty-one cartridges were collected during 2003 and were analyzed for isoprene and individual monoterpenes. Table 1 shows the description of the 2002 and 2003 campaigns and sampling strategies. The sampling protocol of 2003 is similar to that used in 2002. Plots 2 and 3 were within 50 m of plot 1. The dominant plant species in each plot are shown in Table 2.

3. Results and discussion

Isoprene and monoterpene emissions were measured from a grassland landscape that includes bare soil, grasses (e.g., *Aneurolepidium*), sedges (*Carex*), and forbs (e.g., *Artemisia*). Fifty-five enclosure measurements were made on a single sampling plot in order to examine diurnal, seasonal and interannual variability in isoprene emission rates. Additional measurements were used to characterize spatial variations.

Table 1
Description of sample plots, sampling methods, number of samples (N) and normalized (temperature = 30 °C, PPFD = 1500 μmol $m^{-2}s^{-1}$) mean and standard error of the mean (in parenthesis) isoprene and monoterpene emission rates (μg $m^{-2}h^{-1}$)

Year	Sampling periods	Sampling plot	Sampling method	N	Grazing intensity	Vegetation cover (%)	Biomass density (g m^{-2})	Normalized isoprene emission Rate	Normalized monoterpene emission rate
2002	June	Plot 1	Canister	15	None	82	Not measured	520 (53)	Not measured
2002	Aug.	Plot 1	Canister	20	None	93	Not measured	490 (24)	Not measured
2002	Sep.	Plot 1	Canister	10	None	80	Not measured	380 (27)	Not measured
2003	Sep.	Plot 1	Cartridge	10	None	89	Not measured	84 (19)	1.6 (0.5)
2003	Sep.	Plot 2	Cartridge	5	None	80	170	50 (37)	1.7 (0.5)
2003	Sep.	Plot 3	Cartridge	5	None	85	200	69 (29)	0.5 (0.06)
2003	Sep.	Plots 4–11	Cartridge	8	Heavy	46	125	81 (21)	0.24 (0.06)
2003	Sep.	Plots 12–14	Cartridge	3	Moderate	71	293	66 (20)	0.2 (0.01)

Table 2
Plant species composition (%) of selected sampling plots

Name	Vegetation cover	*Aneurolepidium Chinense*	*Stipa grandis*	*Achnatherum sibiricum*	*Koeleria cristata*	*Carex appendiculata*	*Cleistogenes squarrosa*	*Allium tenuissimum*
Plot 1	89	4.5	6.3	27.0	0.0	27.0	0.0	13.5
Plot 2	80	23.9	13.0	9.5	15.0	0.5	13.3	1.0
Plot 3	85	11.1	19.0	3.5	4.3	10	5.3	18.9

Fukui and Dosky (1998) and Kirstine et al. (1998) investigated biogenic VOC emissions from temperate grasslands in the North Central US and South Central Australia, respectively, and observed total terpenoid emission rates that range from <1 to $\sim 80\,\mu g\,m^{-2}\,h^{-1}$ but were less than $10\,\mu g\,m^{-2}\,h^{-1}$ in most cases. The highest rates were composed mostly of monoterpenes and were associated with flowering (Fukui and Dosky 1998). Klinger et al. (1994); Isebrands et al. (1999) and Janson and de Serves (2001) examined emissions from ground cover (grasslands and bogs) at higher latitudes and observed substantial emissions of isoprene ($>2000\,\mu g\,m^{-2}\,h^{-1}$) and monoterpenes ($>500\,\mu g\,m^{-2}\,h^{-1}$). In comparison, forest emissions typically range from about 1500 to $20000\,\mu g\,m^{-2}\,h^{-1}$ of isoprene and from 300 to $1500\,\mu g\,m^{-2}\,h^{-1}$ of monoterpenes (Guenther et al., 1995). Our estimates of isoprene emissions for the four campaigns in Inner Mongolia were normalized to an above-canopy temperature of 30 °C and PPFD of $1500\,\mu mol\,m^{-2}\,s^{-1}$ using the model of Guenther et al. (1999) and ranged from 50 to $520\,\mu g\,m^{-2}\,h^{-1}$ for different plots and seasons. These values fall between the isoprene emissions reported for temperate grasslands (Fukui and Dosky 1998; Kirstine et al., 1998) and those observed for northern ground cover vegetation (Klinger et al., 1994, Isebrands et al., 1999). Total monoterpene emissions, normalized to a temperature of 30 °C, ranged from 0.2 to $1.7\,\mu g\,m^{-2}\,h^{-1}$. These very low emission rates are at the lower end of the range of grassland monoterpene emission rates reported by Fukui and Dosky (1998) and Kirstine et al. (1998). Limonene and carene each contributed about 37% of the total monoterpene emissions with most of the remainder consisting of α-pinene and β-pinene.

A sampling plot with only bare ground (without vegetation) was examined and the results show that the soil was not a significant source or sink of these compounds. The average normalized isoprene emission rate, for all sampling plots containing vegetation, in September 2003 was $59\,\mu g\,m^{-2}\,h^{-1}$, with a range of 2 to $221\,\mu g\,m^{-2}\,h^{-1}$. The vegetation covered fraction of these plots ranged from 30% to 100% and the foliar biomass ranged from 38 to $350\,g\,m^{-2}$. There was no correlation between isoprene emission and total foliar biomass, probably because only a small fraction of the plant species was responsible for the isoprene emission. The observations shown in Tables 1 and 2 demonstrate that there was a strong positive correlation between isoprene emission and the presence of *C. appendiculata* in the sampling plots. Although other species may have also contributed to the total isoprene emission, it appears that this species could be an important source of isoprene emission from this grassland.

Fig. 1 demonstrates that isoprene emission is correlated with temperature and PPFD variations and generally follows the relationship described by the canopy model of Guenther et al. (1999, 2006). The considerable scatter observed at high temperatures is expected due to the instability of isoprene emission rates at high temperatures (Guenther et al., 1993). The continued increase in isoprene emissions with increasing PPFD indicates that a canopy model should be used for estimating these grassland emissions rather than a big leaf model (Guenther et al., 2006). A significant seasonal variation in the daily isoprene emission rate for plot 1 was observed with emissions decreasing from June through September in 2002. Differences in light and temperature during the measurement periods contributed to the observed variations. When the algorithms of Guenther et al. (2006) were used to normalize whole canopy emissions to standard light and temperature conditions, the June and August fluxes were both $\sim 500\,\mu g\,m^{-2}\,h^{-1}$ while the average September flux was ~25% lower.

The normalized isoprene emissions observed from plot 1 in September 2003 were about 75% lower than the rates in September 2002. Precipitation, which was exceptionally high during 2002, was

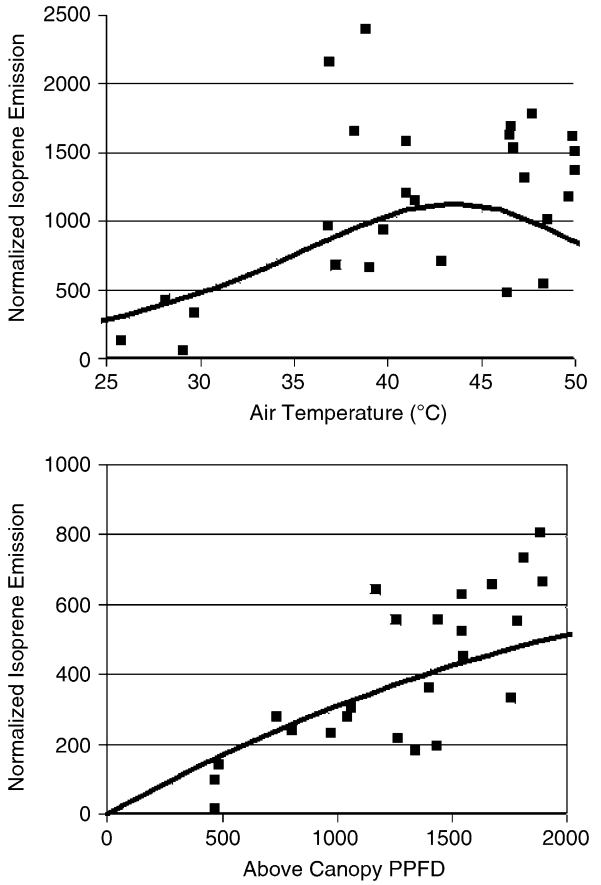

Fig. 1. Observed and predicted relationship of isoprene emission rates ($\mu g\,m^{-2}\,h^{-1}$) with temperature (top) and PPFD (bottom). The observations (squares) include all June and August 2002 measurements. The isoprene emission rates in the top panel were normalized for PPFD ($= 1500\,\mu mol\,m^{-2}\,s^{-1}$) and in the bottom panel for temperature (30 °C) using the canopy model of Guenther et al. (2006). Emission variations simulated using the canopy model of Guenther et al. (2006) is shown (solid line) for reference.

notably different between these years. However, the precipitation rates during the first 10 days of September of 2002 and 2003 were similar and so there may have been little difference in soil moisture during the September 2002 and 2003 measurement periods. Because plot 1 was an undisturbed plot that was not harvested during the two year experiment, there are no direct biomass measurements. However, there was no noticeable difference in biomass in September 2002 and 2003. Note that we cannot eliminate the possibility that the different sample storage and analytical methods used in 2002 and 2003 could have contributed to the difference.

The sensitivity of regional isoprene emission estimates to the emission factors assigned to grass and other groundcover was investigated using the Model of Emissions of Gases and Aerosols from Nature (MEGAN) emission model (Guenther et al., 2006). The sensitivity of MEGAN emission estimates to the isoprene emission factor used for grass and ground cover was examined using the following three factors: $3\,\mu g\,m^{-2}\,h^{-1}$ (based on Kirstine et al., 1998 and Fukui and Doskey, 1998), $400\,\mu g\,m^{-2}\,h^{-1}$ (based on this work) and $1200\,\mu g\,m^{-2}\,h^{-1}$ (based on groundcover measurements of Klinger et al., 1994 and Isebrands et al., 1999). We selected a value of $400\,\mu g\,m^{-2}\,h^{-1}$ to represent the emissions from our Inner Mongolia grassland site, which were $\sim 500\,\mu g\,m^{-2}\,h^{-1}$ in summer 2002 but were lower in 2003. We conducted the model sensitivity tests using eight different landcover databases, described by Guenther et al. (2006), which have spatial resolutions ranging from $\sim 1\,km^2$ to 1° latitude × 1° longitude. The results varied somewhat for different landcover databases but generally showed that uncertainties in isoprene emission factors for grass and other ground cover is a significant component (~5%) of the total uncertainty associated with isoprene emission estimates for China. The estimated contribution of grass, sedges, herbs and mosses to the total annual isoprene emissions from China increased from <0.05% for the lowest emission factor to 4–12% for the higher emission factors. The grass contribution to global scale emissions was about a factor of three lower, (<0.02% to 4%) and the contribution to Inner Mongolia was more than a factor of three higher (<0.2% to >40%). These results indicate that grass and other herbaceous vegetation make a very small contribution to global scale isoprene emissions but can be important in some regions.

4. Summary and Conclusions

Isoprene and monoterpene emissions from an Inner Mongolia grassland were investigated using enclosure measurement methods. Summertime emissions of $\sim 500\,\mu g\,m^{-2}\,h^{-1}$ observed in 2002 are much higher than values reported for temperate grasslands by Fukui and Doskey (1998) and Kirstine et al. (1998) but are lower than those reported for ground vegetation at higher latitudes by Klinger et al. (1994) and Isebrands et al. (1999). This wide range of observed emissions demonstrates that a single emission factor for grass and other ground vegetation is not sufficient for global modeling.

The observed response of isoprene emission to changes in temperature and solar radiation transmission at this grassland site can be simulated using the canopy emission model described by Guenther et al. (1999). Observed seasonal variations result in 25% lower isoprene emissions in September than in June or August. Substantial interannual variations (75%) were observed but were not demonstrated conclusively due to a change in analytical methods. Spatial variations in isoprene emissions, for plots that had various levels of grazing intensity, did not correlate with total biomass density but were correlated with the biomass density of the sedge, *C. appendiculata*, which may be a significant isoprene source in this region.

Monoterpene emissions were very low ($\sim 3\,\mu g\,m^{-2}\,h^{-1}$). Normalized isoprene emissions ($50–500\,\mu g\,m^{-2}\,h^{-1}$) were higher than what has been observed in other grasslands but are still lower than what has been observed for ground cover in other regions. Isoprene emitted from ground cover vegetation (sedges, moss, herbs, etc.) probably makes a negligible contribution to the global annual total but is important for some regions and should be better characterized. Future studies are needed to quantify above canopy fluxes of seasonal and interannual variations as well as measurements characterizing the contribution of individual vegetation species.

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