

Influence of Soil Moisture on Isoprene Emissions From a Northern Mixed Hardwood Forest

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Abstract

The objective of this study was to identify a relationship between soil moisture and isoprene emissions and treat the variables in a manner that could be compared with the Model of Emissions for Gases and Aerosols in Nature model's (MEGAN) treatment of changes in soil moisture as a factor affecting emissions of isoprene. Soil moisture data and isoprene flux measurements from a northern mixed hardwood forest in northern Michigan were studied for the 2000-2005 growing seasons. The two variables were examined using the parameters from the MEGAN model where soil moisture emission activity factors, calculated from observed soil moisture measurement data, were compared to observed isoprene fluxes normalized for photosynthetic photon flux density, temperature, and light. Variability in the trends was observed between the individual years showing positive, negative and no relationships. The results demonstrate that there is no relationship between soil moisture and isoprene emissions.

INTRODUCTION

Considered among one of the most significant atmosphere-biosphere interactions (Sharkey et al. 2001), the production and emission of isoprene (2-methyl-1,3-butadiene) from vegetation has a profound influence on atmospheric chemistry (Guenther et al. 2000). For North America isoprene annual emissions are estimated to be 29 Tg C/yr, which is 35% of total biogenic volatile organic compounds (BVOC) emissions, and which is comparable to anthropogenic VOC emissions (Guenther et al. 2000). In NO_x-rich environments, such as the eastern U.S., photochemical oxidation of VOCs (including isoprene) can increase ozone (O₃) concentrations by 20-80% (Pierce et al. 1998). On a global scale oxidation of isoprene with a hydroxyl radical modifies the atmosphere's oxidative capacity resulting in longer atmospheric residence times for methane (CH₄), which is an important greenhouse gas. Isoprene can also produce small amounts of secondary organic aerosols, which have implications for climate change (ref.). As a result, the development and evaluation of biogenic emission models is a critical aspect for managing air quality and for understanding global climate change.

Accurate measurements of BVOC emissions are needed for regional atmospheric chemistry and climate models. Biogenic isoprene is a hemiterpene made from dimethylallyl pyrophosphate (DMAPP) by the enzyme isoprene synthase (Silver and Fall 1991). Isoprene emission is influenced by both environmental and physiological processes. And in contrast to many other VOCs produced by plants, isoprene is not stored within specialized storage organelles (Monson et al. 1995); but rather, isoprene upon synthesis diffuses from within the chloroplast and leave out through the stomata of the leaf epidermis (Lerdau 2007). Through a combination of laboratory and field studies the patterns and magnitudes of isoprene emission have been determined for a wide variety of plant species (Guenther et al. 2000). It is well known that isoprene emissions only occur during the day and the emission rate is strongly dependent on light and temperature (Sanadze 1969;Guenther et al. 1993). At 30°C isoprene emission rates can be as high as 100 $\mu\text{g}/\text{m}^2/\text{h}$ for deciduous species such as oak and aspen (ref.). Isoprene is emitted from a number of deciduous species including oak, aspen, eucalyptus, and for conifers only from spruce (ref.).

While research has established an important role for isoprene in biosphere-atmosphere interactions, it is unclear why isoprene is produced and emitted by plants. There are currently three competing hypotheses for why plants emit isoprene. The first postulates that isoprene allows for thermotolerance protecting the plant against short high-temperature episodes (Sharkey and Singaas 1995). The second hypothesis proposes that isoprene serves as an antioxidant protecting the plant against detrimental exposure to ozone (Sharkey 2001), and the third suggests that isoprene emission serves as a route for releasing excess carbon and energy (Logan et al. 2000 as cited in Sharkey 2001). In addition to that critical question, there remains a gap in knowledge regarding our understanding of the relationships affecting isoprene behavior. Recent temperature history, shaded and sunlit leaves, time within the growing season, and soil moisture are among a number of environmental factors for which the influences on isoprene emission remain unclear. A greater understanding of isoprene emissions and its relationship to a number of environmental factors is critical for generating models with improved ability to predict isoprene emissions and impacts on photochemistry.

Measurements of isoprene emissions have been made using leaf or branch enclosure techniques (ref.), and at the canopy scale, using eddy covariance methods (Guenther and Hills 1998; Westberg et al. 1998; Pressley et al. 2005). The canopy scale eddy flux measurements are particularly valuable for linking leaf level dynamics to regional scale emissions. Pressley et al. made measurements over a northern hardwood forest using eddy flux techniques covering four growing seasons (1999-2002). This flux record now extends into 2007.

Our understanding of leaf level emissions has been incorporated into emission inventory models as a basis for treating isoprene within regional and global scale photochemical modeling systems. Two current emission inventory models include the USEPA Biogenic Emission Inventory System 3 (BEIS3) (Pierce et al. 2002) and the Model of Emissions of Gases and Aerosols from Nature (MEGAN) (Guenther et al. 2006). Pressley et al. (2005) employed long-term above canopy isoprene flux measurements to evaluate the performance of BEIS3. The results showed that BEIS3 estimates agreed well with observations during the midsummer period but BEIS3 overestimates observations during the spring onset and fall decline of emissions (Pressley et al. 2005). Predictions with the BEIS3 model yielded fractional errors ranging from 31%-65% (Pressley) – showing that current models do not correctly capture all of the variability associated with observed isoprene fluxes.

In the MEGAN model Guenther and colleagues have developed a framework to treat a large number of environmental factors that can affect emissions. For example, the effects of soil moisture are incorporated through relationships between stomatal conductance and soil moisture and also through an empirical emission activity factor that is a function of soil moisture. However, for soil moisture and other environmental parameters there have been no comprehensive evaluations of the MEGAN model. Predicted isoprene fluxes (MEGAN) are plotted versus observed isoprene fluxes in Figure 1. In some years (2001, 2002, 2005) predicted and observed fluxes are in fairly to very good agreement. However, in other years (2000, 2003, 2004) there significant disagreement and it is not clear why MEGAN's ability to predict isoprene emissions is so variable.

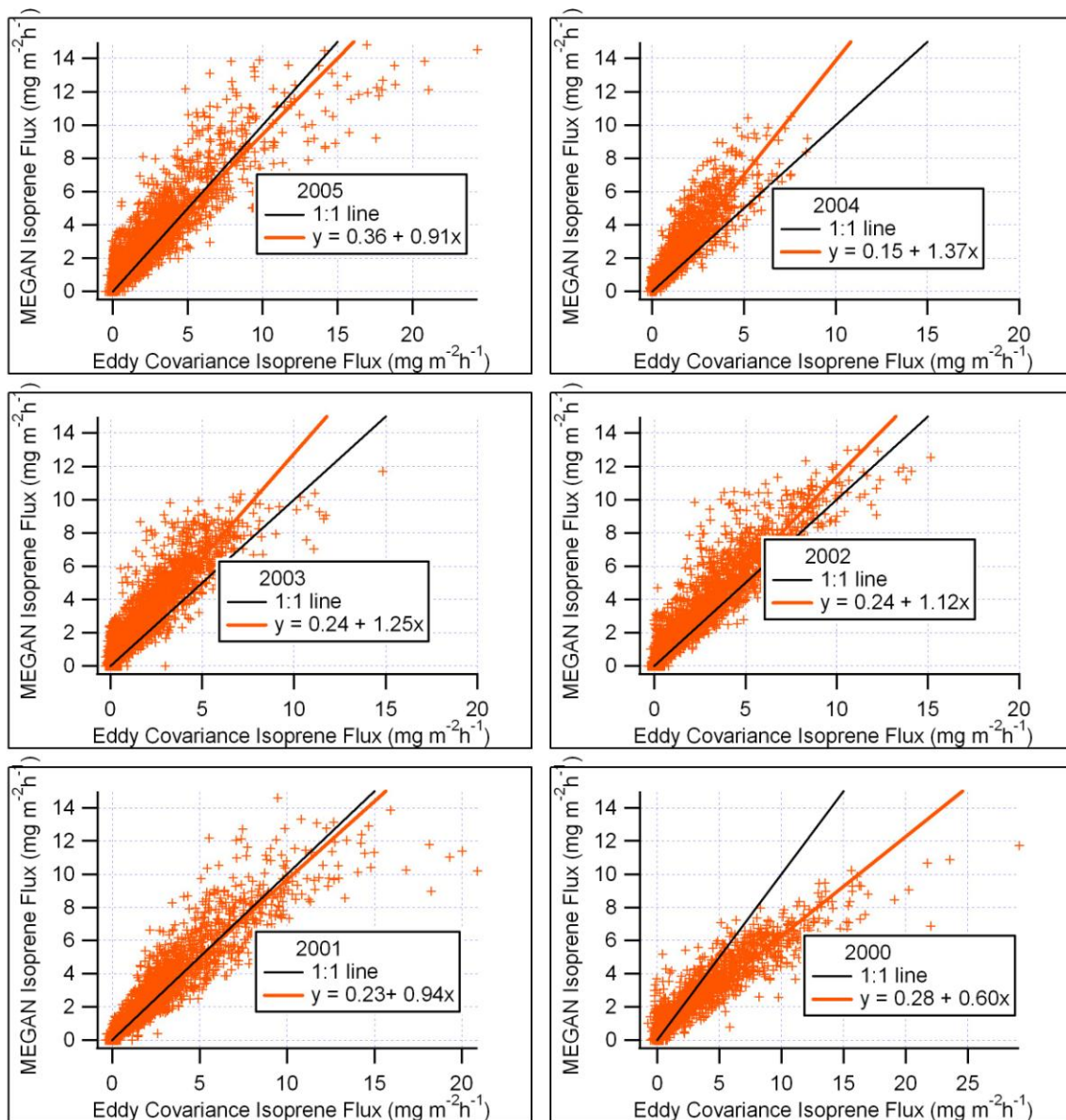


Fig. 1. Year to year comparison of MEGAN predictions of isoprene flux with observed isoprene fluxes for a mixed northern hardwood forest located in northern Michigan.

Goals and Hypotheses

The overall goal for this work is to improve our understanding of isoprene emissions and improve our ability to accurately model isoprene emissions for regional and global chemical modeling. Specifically, we investigate the relationship of soil moisture and isoprene emissions; and investigate the relative importance of stomatal and non-stomatal emissions of isoprene. We used the available continuous isoprene flux data from the PROPHET Tower site and UMBS Flux data to evaluate the relationship of soil

moisture and isoprene emissions in a manner that can be compared with the MEGAN's treatment of soil moisture. Based on MEGAN's treatment of soil moisture we expect decreased soil moisture will correspond to decreased isoprene emissions.

METHODS

Research Site

The measurements for this research were collected from the University of Michigan Biological Station located in northern Michigan (45°30'N, 84°42'W). The flux system is set up at the PROPHET Tower (the Program for Research on Oxidants: PHotochemistry, Emission, and Transport (Carroll et al. 2001), which is 30.5 m in height. The site is situated in a northern hardwood forest with a canopy composed of bigtooth aspen (*Populus grandidentata* Michx.), quaking aspen (*P. tremuloides* Michx.), beech (*Fagus grandifolia* Ehrh.), paper birch (*Betula papyrifera* Marsh.), and red oak (*Quercus rubra* L.). Aspen and oak are the primary emitters of isoprene in this forest and constitute a dominant portion of the biomass surrounding the tower. The average canopy height is 22 m and measurements were made at a height of 32 m. The site is characterized with a soil type of rubicon sand and is excessively drained.

Measurements and calculations

The eddy covariance technique was used to measure isoprene, CO₂, H₂O, and sensible heat fluxes on a continuous basis throughout each growing season. In the eddy covariance technique flux for a particular species is determined from:

$$F = \overline{w'c'}$$

where w' is the fluctuating vertical velocity and c' is the fluctuating concentration and the overbar indicates an average over 30 minutes. In order to capture the effects of small eddies, the fluctuating terms are typically measured at 10 Hz.

The Fast Isoprene Sensor (FIS) (Hills and Zimmerman 1990) was used to measure isoprene and an open-path infrared gas analyzer was used to measure CO₂ and H₂O. A 3-D sonic anemometer was used to measure turbulent velocities and temperature

fluctuations. The data acquisition system for the eddy covariance data was a fast response (10 Hz) system (Pressley et al. 2005) storing data for 30-minute data files.

FIS flux system components:

- Sonic anemometer – wind speed & directions
- Open path Infrared Gas Analyzer (IRGA) – CO₂ and H₂O concentrations
- Fast Isoprene Sensor (FIS) – isoprene concentrations
- Ozone Generator – Converts O₂ to O₃ for the chemiluminescent reaction (FIS)
- Vaisala Relative Humidity (RH) & Temperature Probe
- DataPacker – Converts Analog signal to Digital
- Startech – Converts serial output to ethernet
- Computer – Runs LabVIEW data acquisition software
- TSI Flowmeter (1pm) – measures air flow through the sample line
- Pump – Pulls air from the top of the tower to the base of the tower

The IGOR Flux program was used to process data from the FIS flux system for previous growing seasons to obtain eddy covariance measurements of isoprene. Data processing required manipulation of the raw 10Hz data for each of the 30-minute periods compiled by the FIS flux system. This required 1) calculation and application of calibration coefficients and conversion of the raw digital data to scientific units; 2) calculation of the vertical wind component and the isoprene mixing ratio for a range of times and determination of the daily lag time between the sonic signal and FIS; 3) removal of hard spikes; 4) orientation of u in the mean wind direction; 5) computation of averages and standard deviations for each variable; 6) removal of soft-spikes from vertical wind component based on standard deviation; 7) removal of means to create prime-quantities; 8) calculation of instantaneous fluxes; 9) determination of 30 min-average fluxes for momentum, sensible heat, latent heat, CO₂, and isoprene; 10) correction of isoprene, CO₂ and latent heat fluxes for the effects of density fluctuations; 11) Correction of isoprene flux for high-frequency losses due to transport through the sampling line.

This study employs data from six growing seasons, 2000-2005, collected from both the PROPHET tower and the UMBS Flux tower which is located approximately 100 m north of the PROPHET tower.

Data analysis for soil moisture

MEGAN – Model of Emissions for Gases and Aerosols in Nature

The MEGAN model developed by Guenther et al. estimates the net emission rate ($\text{mg compound m}^{-2} \text{ h}^{-1}$) of isoprene and other trace gases and aerosols into the above-canopy atmosphere from terrestrial ecosystems at a particular time and location as

$$\text{Emission} = [\varepsilon][\gamma][\rho] \quad (1)$$

where ε is the emission factor for a particular compound into the canopy at standard conditions, γ (normalized ratio) is an emission activity that accounts for changes in the emission from deviations from standard conditions¹ and ρ (normalized ratio) is a factor that accounts for within canopy- production and loss of the particular compound. Soil moisture is accounted for in the model indirectly by the soil moisture dependence of stomatal conductance, which affects leaf temperature estimated by the MEGAN canopy environment. MEGAN also accounts for soil moisture with an emission activity factor that is dependent on soil moisture. The soil moisture emission activity factor is one of three terms that constitute the total emission activity factor ($\gamma = \gamma_{\text{CE}} \cdot \gamma_{\text{age}} \cdot \gamma_{\text{SM}}$; canopy environment, leaf age, soil moisture) and it reports variations induced by physiological and phenological processes driving the rates of isoprene emission. The soil moisture emission activity factor is estimated as

$$\gamma_{\text{SM}} = 1 \quad \theta > \theta_1 \quad (20a)$$

$$\gamma_{\text{SM}} = (\theta - \theta_w) / \Delta\theta_1 \quad \theta_w < \theta < \theta_1 \quad (20b)$$

$$\gamma_{\text{SM}} = 0 \quad \theta < \theta_w \quad (20c)$$

¹ The standard conditions for the MEGAN canopy-scale emission factors include a leaf area index, LAI of 5 and a canopy with 80% mature, 10% growing and 10% old foliage; current environmental conditions including a solar angle (degrees from horizon to sun) of 60 degrees, a photosynthetic photon flux density (PPFD) transmission (ratio of sphere) of 0.6, air temperature=303 K, humidity=14 g kg⁻¹, wind speed=3 m s⁻¹ and soil moisture=0.3 m³ m⁻³; average canopy environmental conditions of the past 24 to 240 h include leaf temperature=297 K and PPFD=200 $\mu\text{mol m}^{-2} \text{ s}^{-1}$ for sun leaves and 50 $\mu\text{mol m}^{-2} \text{ s}^{-1}$ for shade leaves

where θ is soil moisture (volumetric water content, $\text{m}^3 \text{m}^{-3}$), θ_w ($\text{m}^3 \text{m}^{-3}$) is the wilting point, a threshold level of soil moisture below which plants are no longer able to extract water from the soil), $\Delta\theta_1$ ($=0.06$) is an empirical parameter based on a study by Pegoraro et al. (2004), and $\theta_1 = \theta_w + \Delta\theta_1$.

To evaluate MEGAN's treatment of soil moisture effects on isoprene emission, soil emission activity factors were calculated for the half-hourly soil moisture data obtained from the UMBS Flux database. A wilting point of 0.01 as assigned by Chen and Dudhia (2001) (Appendix A) was applied for the sand soil type which characterizes the soil at our site.

In order to compare trends between the calculated soil moisture emission activity factors with the observed isoprene flux data, it was necessary to normalize the measured fluxes for light and temperature – two variables that greatly affect the behavior of isoprene emissions. In the MEGAN model changes in light and temperature from standard conditions are accounted for in the emission activity factor for the canopy environment (γ_{CE}). The canopy environment was calculated using the Parameterized Canopy Environment Emission Activity algorithm (PCEEA) rather than the MEGAN canopy environment model because estimates for annual global isoprene emissions using the PCEEA approach are within ~5% of the value generated by the standard MEGAN canopy environment model (Guenther et al. 2006). However, the difference between estimates at specific times and locations can exceed 25% (Guenther et al. 2006). The PCEEA algorithm is the alternative to the detailed canopy environment and estimates the canopy environment activity factor as

$$\gamma_{CE} = \gamma_{LAI} \cdot \gamma_P \cdot \gamma_T \quad (10)$$

where γ_{LAI} , γ_P , γ_T are three terms that account leaf area index (LAI), photosynthetic photon flux density (PPFD), and temperature variations. The response to PPFD variations for canopy scale isoprene emissions is modeled in MEGAN as

$$\gamma_P = 0 \quad a < 0, a > 180 \quad (11a)$$

$$\gamma_P = \sin(a)[2.46(1 + 0.0005 \cdot (P_{\text{daily}} - 400))\phi - 0.9\phi^2] \quad 0 < a < 180 \quad (11b)$$

where P_{daily} is the daily average above canopy PPFD ($\mu\text{mol m}^{-2}\text{s}^{-1}$), a is the solar angle (degrees), and ϕ is the above canopy PPFD transmission. Solar angle was calculated following Campbell and Norman (1998) calculations for the elevation angle (Appendix A). ϕ is calculated from

$$\phi = P_{\text{ac}}/(\sin(a)P_{\text{toa}}) \quad (12)$$

where P_{ac} is above-canopy PPFD (hourly), and P_{toa} is PPFD ($\mu\text{mol m}^{-2}\text{s}^{-1}$) at the top of the atmosphere, which can be approximated as

$$P_{\text{toa}} = 3000 + 99 \cdot \cos(2 \cdot 3.14 \cdot (\text{DOY} - 10)/365) \quad (13)$$

with DOY as the day of year.

The temperature response factor, γ_T , is estimated as

$$\gamma_T = E_{\text{opt}} \cdot C_{T2} \cdot \exp(C_{T1} \cdot x) / (C_{T2} - C_{T1} \cdot (1 - \exp(C_{T2} \cdot x))) \quad (14)$$

where $x = [(1/T_{\text{opt}}) - (1/T_{hr})] / 0.00831$, $E_{\text{opt}} = 1.75 \cdot \exp(0.08(T_{\text{daily}} - 297))$, T_{hr} is hourly average air temperature (K), T_{daily} is daily average air temperature (K), C_{T1} (=80) and C_{T2} (=200) are empirical coefficients, and $T_{\text{opt}} = 313 + (0.6 \cdot (T_{\text{daily}} - 297))$.

The third factor in the canopy environment is LAI which is estimated as

$$\gamma_{\text{LAI}} = 0.49\text{LAI} / [(1 + 0.2\text{LAI}^2)^{0.5}] \quad (15)$$

The LAI values obtained from the UMBS Flux tower were interpolated to obtain half-hourly data over the entire growing season and then used applied in the above equation for computing the LAI response factor.

The PCEEA allowed for the calculation of the canopy environment emission activity factor (γ_{CE}), which was then used to normalize the flux by dividing the observed isoprene flux measurement by this factor. However, due to exceedingly small values of γ_P at dawn, dusk and night, the normalized flux data was filtered for daytime hours 09:00

to 16:30. The normalized fluxes were filtered for the time 09:00 to 16:30 for all days studied during the growing season among the six years and only this data was used in the data analysis presented here.

Time series were plotted to examine normalized fluxes and MEGAN γ_{SM} values over the growing season for each of the studied years. In order to examine soil moisture during times of water stress or drought, data for times when the soil moisture emission activity factors were less than 1 ($\gamma_{SM} < 1$) were evaluated. Best-fit linear regressions were plotted for graphs of normalized fluxes against values of $\gamma_{SM} < 1$. The data was further analyzed by binning the data in two ways and averaging the normalized isoprene fluxes for the individual years and for the six years cumulatively. Normalized fluxes were averaged for the data when $\gamma_{SM} < 1$ and when $\gamma_{SM} = 1$, for days 180 – 260. Normalized fluxes were also averaged for γ_{SM} binned by 0.1 increments. Based on our data, with a minimum γ_{SM} value of 0.4, the data was separated into the following bins with γ_{SM} values of: 0.4 to <0.5, 0.5 to <0.6, 0.6 to <0.7, 0.7 to <0.8, 0.8 to <0.9, 0.9 to <1, and =1.

Stomatal Flux Calculation

The stomatal flux of isoprene was estimated by calculating the product of the stomatal conductance of isoprene (mol/m²/s) and the mixing ratio of isoprene (ppb of C). The stomatal conductance of isoprene was calculated using the equations published by Hogg et al. (2007) (Appendix C) which employed a resistance analog model of gas transfer to calculate stomatal and non-stomatal conductance of ozone. This method determines stomatal conductance based on the ratio of water conductance to the particular compound of interest as a function of the molecular diffusivity dictated by the molecular weight of the compound.

RESULTS

Soil moisture and isoprene emissions

For the 2000-2005 growing seasons we investigated the relationship between soil moisture and isoprene emission. The data was treated in a manner that also allowed us to compare a trend to the MEGAN model by using the equations and parameters developed by the model. The soil moisture emission activity factor was calculated from observed

soil moisture data, and observed isoprene fluxes were normalized for the light, temperature, and LAI as described above.

From the normalized isoprene fluxes and the MEGAN soil moisture emission activity factors shown in Figure 2. it is evident that γ_{SM} is rarely less than 1 in this northern mixed hardwood forest. While γ_{SM} infrequently falls below 1, significant inter-annual variability is seen in the amount of time when γ_{SM} is below 1. Year 2003 displays fewest time periods when γ_{SM} is less than 1, while γ_{SM} is <1 nearly 50% of the time during the 2005 growing season. Fig. 2. Time series of MEGAN soil moisture emission activity and normalized flux values along the growing season for years 2000 – 2005.

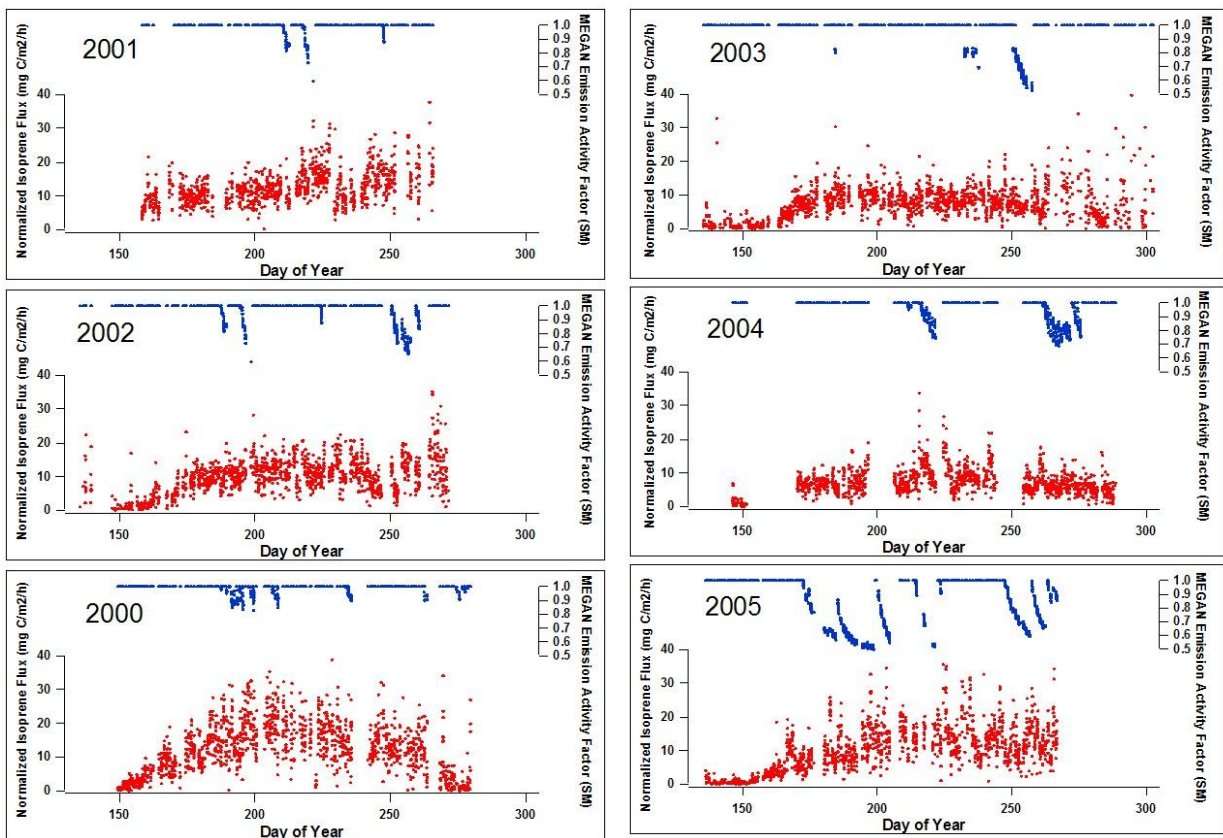


Fig. 2. Time series of γ_{SM} and normalized isoprene fluxes over the growing season during each year.

In order to investigate the effects of isoprene under water-stressed/drought conditions trends with normalized isoprene flux and soil moisture emission activity factors less than 1 analyzed by linear regression for each of the individual years (Fig. 3). Among the six years, five of the years have regressions of statistical significance (2000,

2002, 2003, 2004, and 2005). Years 2000 and 2002 display negative regressions with greater normalized isoprene fluxes corresponding to smaller values of γ_{SM} . Contrastingly, years 2003 and 2004 display positive regressions of greater normalized isoprene fluxes associated with greater values of γ_{SM} . And for 2005, which had the greater number of points ($n = 608$) with $\gamma_{SM} < 1$, there was no relationship between normalized fluxes and γ_{SM} .

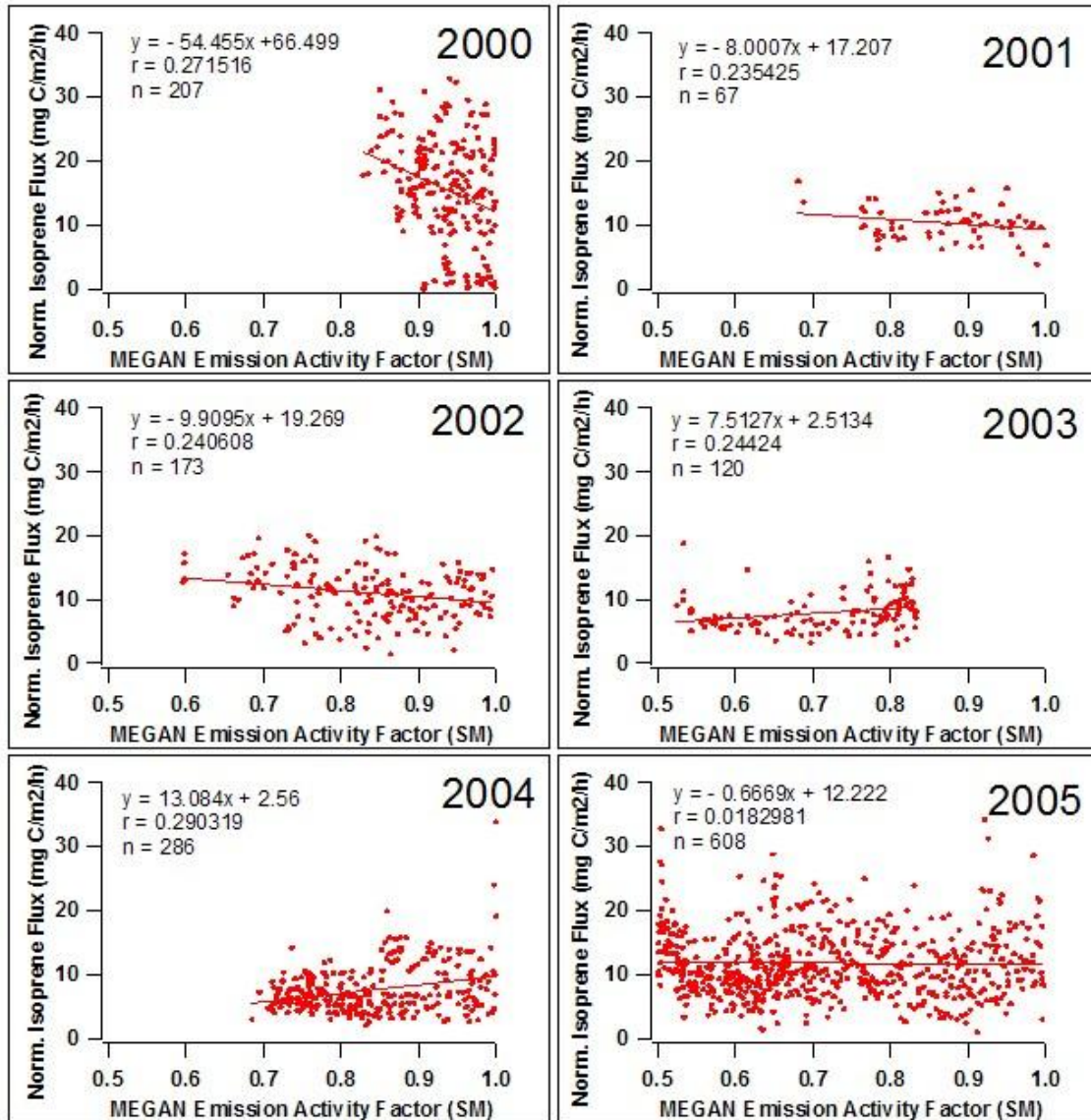


Fig.3. Best fit regression of normalized isoprene fluxes for γ_{SM} values less than 1.

The averaged normalized isoprene fluxes for points when $\gamma_{SM} = 1$ and for points when $\gamma_{SM} < 1$ are presented in Table 1 for each year. There is between year variability but

the variability is not significant. Normalized fluxes for γ_{SM} values equal to one and less than one were fairly comparable for all of the years and showed no significant difference.

Table 1. Average normalized flux (mg C/m²/h) for γ_{SM} values equal to 1 and γ_{SM} values less than 1.

| | Average Normalized Flux (mg C/m ² /h) | |
|--------------------|--|---------------------------|
| | ($\gamma_{SM} = 1$) (n) | ($\gamma_{SM} < 1$) (n) |
| 2000 | 15.5 ± 6.2 (643) | 18.2 ± 6.5 (168) |
| 2001 | 13.3 ± 4.8 (702) | 10.1 ± 2.7 (58) |
| 2002 | 11.0 ± 3.7 (733) | 11.0 ± 4.1 (159) |
| 2003 | 8.9 ± 3.7 (789) | 7.9 ± 3.0 (120) |
| 2004 | 8.1 ± 5.9 (625) | 10.4 ± 4.4 (101) |
| 2005 | 14.5 ± 5.0 (351) | 12.1 ± 5.3 (487) |
| Cumulative '00-'05 | 11.9 ± 5.3 (3843) | 11.6 ± 5.7 (1093) |

Year to year trend variation between the normalized isoprene fluxes and γ_{SM} are again present when binning the γ_{SM} by 0.1 intervals. Table 2 displays both the average normalized flux and the number of points used for averaging the flux for each of the binned intervals. It is important to note that the number of points within some of the bins was considerably small and as a result the corresponding averaged normalized isoprene flux may not be representative of the isoprene flux for the particular γ_{SM} interval. The data from the years cumulatively demonstrate that there no evident trend between the average normalized isoprene fluxes and the emission activity factor for soil.

Table 2. Average normalized isoprene flux values for 0.1 intervals of γ_{SM} .

| Average Normalized Isoprene Flux (mg C/m ² /h) (N) | | | | | | | |
|---|-------------|------------|------------|------------|-----------|------------|----------------------|
| γ_{SM} | 2000 | 2001 | 2002 | 2003 | 2004 | 2005 | Cumulative 2000-2005 |
| 0.4 -0.5 | | | | | | 7.6 (3) | 7.6 (3) |
| 0.5 - 0.6 | | | 14.7 (4) | 7.5 (22) | | 11.9 (159) | 11.4 (185) |
| 0.6 - 0.7 | | 15.1 (2) | 13.7 (14) | 6.5 (30) | 5.1 (2) | 11.7 (164) | 11.1 (212) |
| 0.7 - 0.8 | | 10.2 (13) | 11.5 (41) | 8.3 (36) | 6.8 (107) | 12.3 (101) | 9.6 (298) |
| 0.8 - 0.9 | 18.7 (48) | 10.5 (24) | 10.3 (64) | 8.9 (32) | 7.3 (103) | 10.0 (91) | 10.4 (362) |
| 0.9 - 1 | 14.8 (159) | 9.7 (28) | 10.4 (50) | | 9.2 (74) | 12.9 (90) | 12.4 (401) |
| 1 | 11.9 (1098) | 12.6 (946) | 9.7 (1122) | 7.9 (1441) | 7.2 (959) | 8.5 (749) | 9.6 (6315) |

Stomatal Flux

The calculations computed for the stomatal flux of isoprene were unreasonably small, which has caused us to reconsider the values calculated and whether these values can be considered as representative of stomatal and non-stomatal isoprene emissions.

DISCUSSION and CONCLUSION

Soil moisture and isoprene emissions

The influence of a number of environmental factors on isoprene emission remains unclear. Soil moisture is a variable that is believed to have an effect on isoprene emissions. However, we do not fully understand the relationship may vary in time currently and how it may vary in time in the future as temperature increases. The investigation of how soil moisture affects isoprene emissions as dealt with by the parameters of the MEGAN model, allow for comparison with what is expected from the MEGAN model. and whether there is a common relationship for soil moisture and isoprene developed within the model with the observations measured in the environment.

Based on the treatment of soil moisture by MEGAN we should expect to observe decreased isoprene emissions in relation to decreased soil moisture. However, the result of our study do not a relationship between soil moisture and isoprene emissions. The results of this study show a considerable amount of variation between individual years. With the analysis by best-fit linear regression and analysis by binning γ_{SM} in increments of 0.1 to calculate the average normalized flux, there was a considerable amount of variation between the years that can not clearly support a particular trend that is associated with soil moisture and isoprene emissions. Data from the six years cumulatively demonstrated no relationship as shown by the average normalized fluxes as calculated by the binning of data by 0.1 increments. Binning the data γ_{SM} equal and less than 1 also demonstrated no significant difference to support there is no relationship between soil moisture and isoprene emissions.

Although the results of our study are not consistent with MEGAN's treatment of soil moisture there is substantial inter-annual variability that encourages further investigation. In the inter-annual overlaps, the instantaneous relationship between isoprene emission and soil moisture was studied. However realistically, it is much more likely that isoprene emissions to changes in soil moisture cause change after a period of hours or day. For that reason it is important to look at a lag time that may be associated with isoprene emission response to changes in soil moisture conditions, which has been discussed by Pressley et al. (2006). And to gain a stronger understanding of the

contribution of the soil moisture emission activity factor on isoprene emissions, it would be of interest to have the MEGAN model run predictions for the UMBS forest without setting γ_{SM} at standard conditions (as has already been done) but rather account for soil moisture variability in the predictions. Having these predictions generated by the MEGAN model can allow for greater understanding of the potential contribution that soil moisture has on overall isoprene emissions. It would also be of interest to look at the effects of soil moisture on isoprene emission and eliminating the influence of temperature and light by binning the data by temperature and light conditions and then looking at the soil moisture variability on isoprene fluxes.

It is necessary to continue research on the myriad of environment factors that contribute to the behavior of isoprene emissions. Guenther and colleagues (2006) state that although many laboratory studies included in the development of the model have contributed to the improvement of simulating regional and global isoprene emissions, “it should be recognized that the results continue to be based on a very limited set of observations relative to the large variability that occurs in the earth system.”

Stomatal Flux

The calculations were initiated for obtaining the stomatal flux of isoprene but the final values produced were unreasonably small and suggest that further work needs to be carried out on the calculations. The fraction of stomatal to non-stomatal flux of isoprene would be of great interest and significance for understanding isoprene emissions thus the issues involved with the calculations need to be resolved.

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Appendix A

Wilting point database developed by Chen and Dudhia (2001) and employed by the MEGAN model

| Soil Type | Θ_w (m³ m⁻³) |
|---------------------|---|
| 1 Sand | 0.01 |
| 2 Loamy sand | 0.028 |
| 3 Sandy loam | 0.047 |
| 4 Silt loam | 0.084 |
| 5 Silt | 0.084 |
| 6 Loam | 0.066 |
| 7 Sandy clay loam | 0.067 |
| 8 Silty clay loam | 0.12 |
| 9 Clay loam | 0.103 |
| 10 Sandy clay | 0.1 |
| 11 Silty clay | 0.126 |
| 12 Clay | 0.138 |
| 13 Organic material | 0.06 |
| 14 Water | |
| 15 Bedrock | 0.094 |
| 16 Other (land-ice) | 0.028 |

Equations used for calculating the solar angle (α) applied in the PFD factor in the canopy environment emission activity factor

Equations from Campbell and Norman (1998):

Elevation angle (β) and zenith angle (ψ) are calculated as

$$\cos \psi = \sin \beta = \sin \varphi \sin \delta + \cos \varphi \cos \delta \cos[15(t-t_0)] \quad (11.1)$$

where φ is the latitude, δ is solar declination, t is time in hours, standard local time (ranging from 0 to 24), and t_0 is the time of solar noon.

Solar declination determined by

$$\sin \delta = 0.39785 \sin[278.97 + 0.9856J + 1.9165 \sin(356.6 + 0.9856J)] \quad (11.2)$$

where J is the calendar day (Julian Day).

The time of solar noon is calculated from standard meridian as

$$t_0 = 12 - LC - ET \quad (11.3)$$

where LC is the longitude correction, LC is + 4 minutes, or + 1/15 hour for each degree east of the standard meridian and -1/15 hour for each degree west of the standard meridian; and ET is the equation of time. ET is a 15 to 20 minute correction which depends on calendar day that can be calculated from

$$ET = \frac{-104.7 \sin f + 596.2 \sin 2f + 4.3 \sin 3f - 12.7 \sin 4f - 429.3 \cos f - 2.0 \cos 2f + 19.3 \cos f}{3600} \quad (11.4)$$

where $f = 279.575 + 0.9856J$, in degrees.

Calculating stomatal and non-stomatal conductances for O₃:

1. Calculate diabatic correction factors, ψ_m and ψ_H

$$\zeta = -\frac{0.4gzH}{\hat{\rho}c_pTu^{*3}} \text{ (Campbell 1998, eqn 7.21)}$$

Do not report if $u^* < 0.3$

For unstable ($H > 0$):

$$\Psi_H = -2 \ln \left[\frac{1 + (1 - 16\zeta)^{1/2}}{2} \right] ;$$

$$\Psi_m = 0.6\Psi_H \text{ (Campbell 1998, eqn 7.26)}$$

For stable ($H < 0$):

$$\Psi_m = \Psi_H = 6 \ln(1 + \zeta) \text{ (Campbell 1998, eqn 7.27)}$$

2. Calculate turbulence layer conductance, g_a

Calculate g_a from measurements of $u(z)$ and u^* (Coe et al., 1995, p.1414)

$$r_a = \frac{\overline{u(z)}}{u^{*2}}$$

Do not report if $u^* < 0.3$ or $u(z) < 0.3$

$$g_a = \frac{1}{r_a} \quad \left(\text{in } \frac{m}{s} \right)$$

to convert to $\frac{mol}{m^2s}$, multiply g_a by $\frac{mol}{m^3}$ for air via the ideal gas law

$$\frac{V}{n} = \frac{RT}{P} = \sim 40 \frac{mol}{m^3} \text{ for air}$$

(use V in m³, n in mol, P in Pa, T in K, and R=8.3143 J mol⁻¹ K⁻¹)

3. Calculate boundary layer conductance, g_b

$$\overline{g_b} = \left(\frac{2a}{\alpha}\right) \sqrt{\left(\frac{u(h)}{0.7w}\right)} \left[1 - \exp\left(\frac{-\alpha}{2}\right)\right] \quad (\text{Choudhury et al., 1988, eqn 29})$$

$g_b = \overline{g_b} \cdot LAI$ to express on a ground-area basis

where $u(h)$ is modelled by:

$$u(h) = \frac{u^*}{k} \left[\ln\left(\frac{h-d}{z_m}\right) + \psi_m \right] \quad (\text{Campbell 1998, eqn 7.24})$$

Do not report if $u^* < 0.3$ and set arbitrary minimum $u(h)$ of 0.3 m/s

4. Calculate bulk leaf temperature, T

$$H = c_p g_{Ha} (T_l - T_a) \quad (\text{Campbell 1998, taken from eqn.14.1})$$

and

$$g_{Ha} = \frac{g_a g_b}{g_a + g_b} \quad (\text{in } \frac{\text{mol}}{\text{m}^2 \text{s}})$$

So:

$$T_l = \frac{H}{c_p} \left(\frac{g_a + g_b}{g_a g_b} \right) + T_a$$

g_b must be for heat. So:

$$g_{b-H_2O} = 0.147 \sqrt{\frac{u}{d}} \quad g_{b-heat} = 0.135 \sqrt{\frac{u}{d}} \quad \frac{g_{b-H_2O}}{g_{b-heat}} = \frac{0.147}{0.135} = 1.089$$

This number must be divided by 2, since it is also a matter of heat being dissipated on two sides of the leaf, while water evaporated on one side, the stomatal side. (see C&N eqn 14.2) So:

$$g_{b-heat} = \frac{g_{b-H_2O}}{0.5445} \quad (\text{Campbell 1998, table 7.6})$$

5. Calculate canopy total conductance for water, g_{tot-H_2O}

$$g_{tot-H_2O} = \frac{Ep_a}{VPD} \quad \text{in } \frac{mol}{m^2s} \text{ (Campbell 1998, eqn. 14.10, transposed)}$$

where $VPD = e_s(T_{leaf}) - e_a$

$$e_s(T_{leaf}) = 33.8639 \left[(0.00738T_{leaf} + 0.8072)^8 - 0.000019 \cdot |1.8T_{leaf} + 48| + 0.001316 \right]$$

$$e_s(T_{air}) = 33.8639 \left[(0.00738T_{air} + 0.8072)^8 - 0.000019 \cdot |1.8T_{air} + 48| + 0.001316 \right]$$

$$e_a(T_{air}) = e_s(T_{air}) \cdot \left(\frac{RH}{100} \right)$$

p_a is in kPa

6. Calculate canopy stomatal conductance for water, g_{s-H_2O}

Solve g_s from g_{tot} and g_a and g_b :

$$g_{tot-H_2O} = \frac{1}{r_{tot-H_2O}} = \frac{1}{r_a + r_{b-H_2O} + r_{s-H_2O}}$$

$$r_{s-H_2O} = \frac{1}{g_{tot-H_2O}} - \frac{1}{g_a} - \frac{1}{g_b}$$

Do not report if: $\frac{1}{\frac{1}{g_a} - \frac{1}{g_b}} < 1.25$

7. Calculate canopy surface conductance for ozone, g_{cO_3}

$$F_{O_3} = g_{tot-O_3} mr_{O_3}$$

$$g_{tot-O_3} = \frac{F_{O_3}}{mr_{O_3}}$$

mr_{O_3} is in ppb, F_{O_3} is in $\mu\text{mol}/\text{m}^2/\text{hr}$

$$g_{tot-O_3} = F_{O_3} \cdot \frac{1}{mr_{O_3}} = \frac{\mu\text{mol}}{\text{m}^2\text{hr}} \cdot \frac{\text{mol}}{\text{nmol}} \cdot \frac{1\text{hr}}{3600\text{s}} \cdot \frac{10^9\text{nmol}}{\text{mol}} \cdot \frac{\text{mol}}{10^6\mu\text{mol}} = \frac{\text{mol}}{3.6\text{m}^2\text{s}}$$

units need to be $\frac{\text{mol}}{\text{m}^2\text{s}}$ for fluxes and $\frac{\text{mol}}{\text{mol}}$ for mixing ratio

Solve g_{cO_3} as in step 4 above. The g_{cO_3} is the sum of both stomatal and non-stomatal fluxes. Remember to convert g_{b-H_2O} to boundary layer conductance for ozone according to the molecular diffusivities (section 7.2 and 7.11 and Table 7.4).

Forced convection:
$$\frac{g_{b-H_2O}}{g_{b-O_3}} = \frac{D_{H_2O}}{D_{O_3}} = \left(\frac{1}{\sqrt{\frac{mw_{H_2O}}{mw_{O_3}}}} \right)^{2/3} = \left(\frac{1}{\sqrt{\frac{18}{48}}} \right)^{2/3} = 1.39$$

$$g_{b-O_3} = \frac{g_{b-H_2O}}{1.39}$$

$$g_{tot-O_3} = \frac{1}{r_{tot-O_3}} = \frac{1}{r_a + r_{b-O_3} + r_{c-O_3}}$$

$$r_{c-O_3} = \frac{1}{g_{tot-O_3}} - \frac{1}{g_a} - \frac{1}{g_{b-O_3}}$$

Do not report if:
$$\frac{\frac{1}{g_{tot-O_3}}}{\frac{1}{g_a} - \frac{1}{g_{b-O_3}}} < 1.25$$

8. Calculate $g_{\text{non-s-O}_3}$

Note that g_s for water must be converted to conductance for ozone according to the molecular diffusivities (section 7.2 and 11 and Table 7.4).

$$\text{Molecular diffusion: } \frac{g_{s-H_2O}}{g_{s-O_3}} = \frac{D_{H_2O}}{D_{O_3}} = \frac{1}{\sqrt{\frac{mw_{H_2O}}{mw_{O_3}}}} = \frac{1}{\sqrt{\frac{18}{48}}} = 1.63$$

$$g_{s-O_3} = \frac{g_{s-H_2O}}{1.63}$$

The $g_{\text{non-s-O}_3}$ is calculated as the residual, $g_{\text{non-s-O}_3} = g_{c-O_3} - g_{s-O_3}$

| Variables | | |
|-----------------------------|-------------------------------------|--|
| T_a | C | air temperature at eddy flux measurement height |
| H | W m ⁻² | sensible heat flux |
| RH | dimensionless | relative humidity |
| e_s | kPa | saturation vapor pressure |
| e_a | kPa | vapor pressure |
| p_a | kPa | atmospheric pressure |
| F_{O_3} | mol m ⁻² s ⁻¹ | ozone flux |
| mr _{O₃} | dimensionless | ozone mixing ratio, at eddy flux measurement height |
| E | mol m ⁻² s ⁻¹ | latent heat flux E(gH ₂ O/m ² /s) = E(W/m ² /s)/(2.5e6/1000) (2.5e6 is latent heat of vaporization at 273 K in J/kg) E(mol/m ² /s) = E(gH ₂ O/m ² /s)/mwH ₂ O (mwH ₂ O is 18g/mol) |
| u | m s ⁻¹ | wind speed |
| $u^* = \sqrt{u'w'}$ | m s ⁻¹ | friction velocity |

| Parameters | | | |
|-------------------|-----------------------------------|-------------------------|--|
| R | $\text{J mol}^{-1} \text{K}^{-1}$ | 8.3143 | Gas constant |
| K | dimensionless | 0.4 | Von Kármán's constant |
| LAI | dimensionless | 4.5 | Leaf area index from litter traps |
| $c_p(T,P)$ | $\text{J mol}^{-1} \text{C}^{-1}$ | 29.3 | specific heat of air at constant pressure |
| W | m | 0.08 | leaf width |
| A | $\text{mol m}^{-2} \text{s}^{-1}$ | $1.4*(0.147) = 0.206$ | for water vapor |
| A | $\text{mol m}^{-2} \text{s}^{-1}$ | $2*1.4*(0.135) = 0.378$ | for heat |
| α | dimensionless | 2.5 | attenuation coefficient for wind speed inside the canopy |
| z | m | 35 | measurement height |
| D | m | $0.75h$ | zero plane displacement |
| z_m | m | $0.1h$ | roughness length for momentum |
| H | m | 22 | canopy height |

– Compiled by Alan Hogg, Johan Uddling, and David Ellsworth

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Decimal Day

Wind Speed (m/s)

Wind Direction (degrees)

Friction Velocity (m/s)

Atmospheric Pressure (hPa)

Sonic Temperature (degrees C)

Air Temperature (degrees C)

Relative Humidity (%)

Soil Temperature @ 2 cm depth (degrees C)

PAR (W/m²)

Shortwave Downward Radiation (W/m²)

Net Radiation (W/m²)

Atmospheric CO₂ Concentration (umol/mol)*

Atmospheric Specific Humidity (mmol/mol)

Sensible Heat Flux (W/m²)

Latent Heat Flux (W/m²)

Water Vapor Flux (mmol/m²/s)

NEE (umol/m²/s)

NEE (gap and $u^* < 0.35$ m/s filled by model - umol/m²/s)

Rain @ 46m (mm)

* umol = micromole (μmol)