Estimation of Volatile Organic Compound Fluxes Using the Forest–Land–Atmosphere Model (FLAME)

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(Manuscript received 9 December 1997, in final form 10 June 1998)

ABSTRACT

The prognostic one-dimensional Forest–Land–Atmosphere Model (FLAME) has been further extended to simulate diurnal cycles of volatile organic compound (VOC) fluxes inside and above an idealized mixed forest mainly composed of oaks and pines. The tree height is 12 m and the leaf area index is 4. The canopy crown is divided into five layers of equal leaf area increment. The algorithms developed by Guenther et al. are applied to predict the monoterpene emission from leaves in each canopy layer. The value of photosynthetic active radiation (PAR) and foliage temperature ($T_{\text{leaf}}$) required by these algorithms are provided by FLAME. The modeled PAR and $T_{\text{leaf}}$ are used for different leaf angle classes $i$ from sun to shaded leaves within each layer $j$ in the canopy.

In the present study the authors examine the VOC fluxes modeled at a reference level above the forest for two cases, A and B, for which the modeled canopy temperature $T_c$ reaches a maximum of approximately 21$^\circ$C and 31$^\circ$C, respectively. It is supposed that VOC fluxes above the canopy are related to $T_c$ by a function of the form $F(T_c) = F_s \exp[b_c(T_c - T_s)]$. The authors intend to study the temperature exponent at canopy level $b_c$ by deriving best-fit slopes.

The resulting mean values of $b_c = 0.125 \pm 0.002$ K$^{-1}$ for the morning VOC fluxes, and $b_c = 0.267 \pm 0.004$ K$^{-1}$ for the afternoon, are larger than those used to calculate the emission on leaf scale from cuvette data ($b_1 = 0.124$ K$^{-1}$ and $b_2 = 0.09$ K$^{-1}$ for oaks and pines, respectively). A sensitivity study was carried out using the modeled mean values of $T_{\text{leaf}}$ and PAR in a canopy layer instead of the angle dependence to simulate measurements by an infrared radiation thermometer. The authors also tested the importance of the basal emission rate $E_s$ on the total VOC fluxes and $b_c$ above the canopy.

1. Introduction

Monoterpenes and isoprene are biogenic volatile organic compounds (BVOCs) that are chemically produced inside plants and emitted into the atmosphere. Several studies have demonstrated the role these biogenic components play in ozone chemistry (Chameides et al. 1992; Fehsenfeld et al. 1992; Fuentes et al. 1996) and global carbon budgets (Guenther et al. 1995; Ehhalt et al. 1986). These are among the reasons why increasing attention has been given in the past few years to measuring and modeling BVOCs emission as realistically as possible.

From laboratory measurements it is known that on the leaf level the emission is mainly controlled by leaf temperature and available photosynthetic active radiation (PAR; see Guenther et al. 1991; Guenther et al. 1995). Several authors applied the temperature and light algorithms on leaf basis to compare the measured and modeled diurnal and seasonal course of monoterpene and isoprene emissions under natural conditions (e.g., Bertin et al. 1997; Fuentes et al. 1995; Guenther et al. 1995). Some other authors published data on measured isoprene or monoterpene emission fluxes above canopies determined by micrometeorological and mass budget methods (e.g., Lamb et al. 1985; Schween et al. 1997a; Zelger et al. 1997). In most cases they found that the temperature dependence of these fluxes can be
also parameterized by an exponential function using the Arrhenius relationship. But the temperature exponent $\beta$, expressing the temperature dependence of fluxes measured above canopies seems to be much larger than the exponent calculated from leaf or branch cuvette data. For example the values of $\beta$, found by Schween et al. (1997a) and for data from the Biogenic Emissions in the Mediterranean Area (BEMA) experiment at Castelporziano (see also Seufert et al. 1997) imply that the flux from a pine–oak forest doubles every $2.8^\circ$C, whereas the value proposed by Guenther et al. (1993) would lead to a doubled flux for a change of leaf temperature by $7^\circ$C.

At present BVOC inventories [such as the Biogenic Emissions Inventory System; see Guenther et al. (1995)] describe emission fluxes from forest canopies by relations based on the leaf emission. The temperature exponent is taken to be the same as on the leaf level. Since the interaction of the atmosphere with the canopy is a complex nonlinear process, one would expect the temperature dependence not to be of that simple form. Therefore, a more detailed modeling of forest microclimatology seems to be required in order to obtain reliable estimates of monoterpenes and isoprene emission for various climatic and hydrologic conditions.

In the present study we use the multilayer prognostic Forest–Land–Atmosphere Model (FLAME) to simulate VOC fluxes inside and above a 12-m-tall mixed forest. The original model (Inclán et al. 1996) has been extended to calculate BVOC’s sources (sinks) from each layer in the canopy crown. The BVOC emission rates are calculated for each leaf type (sun to shade) in each canopy layer using the algorithms proposed by Guenther et al. (1993). The required leaf temperature $T_{\text{leaf}}$ and PAR are predicted by FLAME for different leaf orientations from sun to shade leaves. The stand characteristics and general meteorological conditions are taken according to two situations during the BEMA field studies described by Seufert et al. (1997) and Schween et al. (1997b). This study will primarily focus on how to interpret differences found between the temperature exponent at the canopy level, $\beta_c$, and the individual temperature exponents $\beta_s$ and $\beta_o$ (oaks and pines, respectively) determined at leaf level, but will not present further results on detailed analysis of the BEMA-94 campaign (e.g., Seufert et al. 1997).

We examined the best-fit slopes of two case studies, case A and case B, for which the modeled canopy temperature reaches maximum values of approximately 21$^\circ$ and 31$^\circ$C, respectively, and therefore cover variations found in the field during the BEMA campaign during May–June 1994 (e.g., Schween et al. 1997a; Kesselmeier et al. 1997).

In the next sections we give a short description of the monoterpenic algorithms applied for this study. Also the model FLAME is briefly presented. We then show the results on VOC fluxes obtained for two case studies. In addition a sensitivity study using layer averaged values of $T_{\text{leaf}}$ and PAR is presented to point toward the use of $T_s$ for forested areas from remote sensors.

2. Emission from oaks

Emission rates from oaks, $E_{\text{oak}}$, which are found to be mainly dependent on leaf temperature $T_{\text{leaf}}$ and PAR (Seufert et al. 1997), are estimated using the algorithm of Guenther et al. (1993):

$$E_{\text{oak}} = E_{\text{s}}^{\text{oak}} C_{\text{par}} C_T,$$

where $E_{\text{s}}^{\text{oak}}$ is the basal emission rate ($\mu$g m$^{-2}$ s$^{-1}$) at standard temperature $T_s (=303$ K) and standard PAR flux ($1000$ µmol m$^{-2}$ s$^{-1}$). The light dependence factor $C_{\text{par}}$ is defined by

$$C_{\text{par}} = c_{\text{L0}} \frac{c_{\text{L1}} \text{PAR}}{1 + c_{\text{L0}} \text{PAR}^2},$$

where $c_{\text{L0}} (=0.0027)$ and $c_{\text{L1}} (=1.066)$ are empirical coefficients (Guenther et al. 1993), and PAR is the photosynthetic active radiation ($\mu$mol m$^{-2}$ s$^{-1}$) onto a leaf. The response of emission to leaf temperature $T_s$ is calculated by a formula that shows an exponential increase for temperatures below $T_{\text{th}} (=314$ K) with $C_T$ approximated by

$$C_T \approx \exp[\beta_s (T_{\text{leaf}} - T_s)].$$

where $\beta_s (=0.124$ K$^{-1}$) and $T_s (=303$ K) are empirical coefficients estimated from cuvette measurements (e.g., Guenther et al. 1993).

Values of the basal emission rate $E_{\text{oak}}$ are different for each plant type and show seasonal dependence (Seufert et al. 1997; Bertin et al. 1997; Staudt et al. 1997). They are usually determined from cuvette for standard temperature and PAR conditions.

3. Emission from pines

Emission from pines is mainly dependent on leaf temperature:

$$E_{\text{pine}} = E_0^{\text{pine}} \exp[\beta_p (T_{\text{leaf}} - T_s)].$$

Values of the temperature exponent at leaf level $\beta_p$ vary from 0.057 to 0.144 K$^{-1}$ (e.g., Guenther et al. 1993). For the modeling aspects a mean value of $\beta_p = 0.09$ K$^{-1}$ was used as was also obtained from cuvette measurements during BEMA (Seufert et al. 1997). It should be mentioned here that the exponential behavior given by Eq. (4) is assumed to be valid in the temperature range from about 288 to 305 K (Guenther et al. 1993); $E_0^{\text{pine}}$ is the basal emission rate.

4. Short description of FLAME

The fundamentals of the one-dimensional FLAME model have been described in Inclán (1996) and Inclán et al. (1996). For this reason only a brief summary will be given. A simple scheme of FLAME is shown in Fig. 1.
The turbulent and convective exchange between a forested land surface and the atmospheric boundary layer (ABL) is calculated using the first-order nonlocal closure called transient turbulence theory (TTF; Stull 1993). This scheme describes the heat, water, momentum, and mass exchange between all model layers using a nonlocal closure based on a simplified form of the equation for turbulent kinetic energy (TKE). A radiation transfer model within the vegetation (Norman 1979, 1982) predicts the radiation environment for individual classes of leaves throughout the canopy. The canopy is divided into $N$ layers of equal leaf area index increment $\Delta_{LAI}$. The penetration and distribution of radiation within the stand depends mainly on the optical properties of the leaves and the physical structure of the canopy. The visible (400–700 nm) and the near-infrared (700–3000 nm) portions of solar the spectrum are handled separately. In general, leaves are exposed to a wide range of radiation fluxes because of their position and leaf angle distribution. For this reason any leaf process that depends nonlinearly on incident radiation must be described by use of individual leaf angle classes. Therefore the calculation of the leaf energy budget is carried out separately for each angle class $i$ (nine angles for sunlit and one for shaded leaves) and for each layer $j$ within the canopy using

$$\begin{align*}
R_{net,ij} &= \lambda E_{ij} + H_{ij} + \Delta q,
\end{align*}$$

where

$$\begin{align*}
R_{net,ij} &= S_{n,ij}^+ + S_{n,ij}^- + L_{ij} - 2e\sigma T_{leaf,ij}^4, \\
\lambda E_{ij} &= \frac{[e^s(T_{leaf,ij}) - e_{air,j}]}{r_{s,ij} + r_{a,j}}, \quad \text{and} \\
H_{ij} &= \frac{[T_{leaf,ij} - T_{air,j}]}{r_{a,j}}.
\end{align*}$$

The net radiation for an angle class $i$ and a layer $j$ in the canopy is $R_{net,ij}$; $\lambda E_{ij}$, $H_{ij}$ are the turbulent latent and sensible heat fluxes; and $\Delta q$ is the heat stored in the plant material. The downward and upward shortwave radiation fluxes $S_{n,ij}^+$, $S_{n,ij}^-$ as well as the downward longwave radiation flux $L_{ij}$, are calculated by the radiation model. The emissivity of leaves is $\epsilon$ and the Boltzmann constant is $\sigma$. Here, $r_{s,ij}$ and $r_{a,j}$ are the stomata and leaf boundary layer resistances, respectively; $T_{leaf,ij}$ and $T_{air,j}$ are the leaf and air temperatures; and $e^s(T_{leaf,ij})$ and $e_{air,j}$ are the saturation and actual air vapor pressure, respectively. The stomata resistance is parameterized in a way similar to that proposed by Jarvis (1976). The energy balance from Eq. (5) is solved iteratively by guessing $T_{leaf,ij}$ until both sides of the equation are equal. At soil surface a comparable set of equations is solved (see Inclán et al. 1996). Therefore, the fluxes ($R_{net}$, $H$, $\lambda E$, $F$, . . . ) above the forest mostly have contributions from the soil and from the leaves.

Once the energy balance equation has been solved for all angle classes $i$, the average leaf temperature of any layer $j$ in the canopy can be calculated by use of Eq. (6) or

$$\begin{align*}
\bar{T}_{leaf,j} &= \sum_{i=1}^{10} T_{leaf,ij} A_{ij},
\end{align*}$$

where $A_{ij}$ is the fraction of leaf area in any leaf angle class $i$. Values of $A_{ij}$ are calculated by the radiation model.

The transport of heat and water within the soil is computed using the multilayer soil model developed by following Sievers et al. (1983) and Forkel et al. (1984). This model consists of two coupled prognostic equations for the soil temperature and liquid water content. The transport equations include heat conduction, diffusion of liquid water, and water vapor as well as condensation and evaporation of water within the soil pores. For the purpose of our studies a sink term that takes into account the water uptake by roots is included. At the soil surface, soil and atmosphere are connected by balance equations for heat and moisture, including the complete energy budget as in Eq. (5).

FLAME is a prognostic model. For its initialization various input morphological and physiological parameters are required, such as the heights of the canopy and trunk space, the leaf area index, the optical properties of leaves as well as initial profiles of air temperature, humidity, wind, and pressure within the ABL and tem-
temperature and water content in the soil. Once the initialization is completed, a loop over time is carried out to make the forecast.

FLAME predicts vertical profiles of mean meteorological variables and their fluxes within the ABL. The model also forecasts the profiles of temperature and water content in the soil, the corresponding fluxes, as well as leaf temperature, short- and longwave radiation components and stomata resistances for each angle class \( i \) from sun to shade leaves and for each layer within the canopy.

The original model (Inclán et al. 1996) has been further extended to calculate vertical profiles of trace substances like VOCs and their fluxes, \( F_{\text{voc}} \). The VOC sources (sinks) from the vegetation layers are calculated using Eqs. (1) and (4). We take advantage of the detailed light and temperature regime modeled by FLAME within the canopy. The leaf temperature required by Eqs. (3) and (4) is replaced by \( T_{\text{leaf,ij}} \), while the photosynthetically active radiation flux is approximated by the visible radiation flux computed by the radiation model for each canopy layer \( j \) and each angle class \( i \). \( \text{PAR}_{ij} \). The emissions from oaks and pines are estimated using Eqs. (1) and (4) for each time step. The emitted VOCs are then mixed within the ABL using TTT in the same way other passive tracers like water vapor are mixed. From the average concentration of monoterpenes simulated in the canopy space. Hence, the total net flux of any quantity through a level \( k \) is given as the contribution of upward and downward fluxes across the chosen level. The net flux is therefore proportional to the sum of the transient matrix elements multiplied by the corresponding gradients of the specific quantity in all layers below and above the considered level \( k \).

5. Model results

a. Introduction

In the present study we intend to simulate conditions similar to some of those observed during the BEMA project (e.g., Seufert et al. 1997; Kalabokas et al. 1997; Schween et al. 1997a; Schween et al. 1997b).

For representing the forest an idealized tree of 12-m height without understory has been chosen. The trunk height is 6 m, the leaf area index is 4 m² m⁻², and the tree density is set to 400 trees ha⁻¹. We chose a well-watered loamy soil, so that the vegetation has enough moisture in the root zone. The simulation is carried out for Julian day 150 (30 May). Cloud-free sky conditions are chosen. The forest is located at the coordinates 42°N, 12°E.

The vertical model domain from the soil surface up to 3-km height is divided into 45 layers unequally spaced. The idealized tree is divided into 10 layers: 5 within the canopy crown and 5 in the trunk space. We have run FLAME using a unique set of morphological and physiological parameters (Table 1). The downward shortwave radiation at the canopy top is calculated theoretically by the radiation model using the latitude, the day of the year, and time. For the selected day the simulated solar radiation reaches its maximum around midday with a value of 975 W m⁻².

FLAME is initialized at 0500 local time with idealized vertical profiles of air temperature, specific humidity, wind velocity components, and pressure within the ABL as well as temperature and water content in

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( z_f )</td>
<td>Canopy top</td>
<td>12 m</td>
</tr>
<tr>
<td>( z_c )</td>
<td>Trunk height</td>
<td>6 m</td>
</tr>
<tr>
<td>( D_t )</td>
<td>Tree trunk diameter</td>
<td>0.4 m</td>
</tr>
<tr>
<td>LAI</td>
<td>Leaf area index</td>
<td>4</td>
</tr>
<tr>
<td>( \Delta A_l )</td>
<td>Increment of leaf area index</td>
<td>0.80</td>
</tr>
<tr>
<td>( d_l, d_f )</td>
<td>Sides of area corresponding to tree</td>
<td>5 m</td>
</tr>
<tr>
<td>( r_{\text{min}} )</td>
<td>Minimum stomata resistance</td>
<td>120 s m⁻¹</td>
</tr>
<tr>
<td>( r_{\text{cut}} )</td>
<td>Cuticula resistance</td>
<td>2500 s m⁻¹</td>
</tr>
<tr>
<td>( T_{\text{min}}, T_{\text{ir}}, T_{\text{nir}} )</td>
<td>Temperature parameters for stomata</td>
<td>0°, 25°, 35°C</td>
</tr>
<tr>
<td>( \psi_{\text{r}}, \psi_{\text{i}} )</td>
<td>Leaf water potential for stomata</td>
<td>-10, -25 bars</td>
</tr>
<tr>
<td>( r_{\text{min}}, r_{\text{ir}}, r_{\text{nir}} )</td>
<td>Reflection of leaves in VIS, NIR, IR</td>
<td>0.10, 0.50, 0.04</td>
</tr>
<tr>
<td>( \tau_{\text{min}}, \tau_{\text{ir}}, \tau_{\text{nir}} )</td>
<td>Transmission of leaves in VIS, NIR, IR</td>
<td>0.05, 0.30, 0.0</td>
</tr>
<tr>
<td>( r_{\text{cut}}, r_{\text{cut}}^*, r_{\text{cut}}^{**} )</td>
<td>Soil reflection in VIS, NIR, IR</td>
<td>0.08, 0.20, 0.10</td>
</tr>
</tbody>
</table>

Table 1. Some input data for FLAME.
the soil. The initial VOC's profile has been set to zero at all model levels. The model time step is 3 min.

The VOC sources (sinks) from each canopy layer \( j \) are calculated as the VOC contribution from all 10 leaf angle classes \( i \) as follows:

\[
E_{ji}^{\text{oak}} = \sum_{i=1}^{10} E_{ij}^{\text{oak}} A_{ij} \quad \text{and} \quad E_{ji}^{\text{pine}} = \sum_{i=1}^{10} E_{ij}^{\text{pine}} A_{ij},
\]

(11)

The emission from a leaf area with angle class \( i \) in a layer \( j \) for oaks and pines \( E_{ij}^{\text{oak}}, E_{ij}^{\text{pine}} \) is calculated using Eqs. (1) and (4). We use the light-dependent values of leaf temperature \( T_{\text{leaf},ij} \) and PAR predicted by FLAME and make a weight by the fraction of leaves \( A_{ij} \) in each of the leaf angle classes considered. Presently we do not consider VOC emission either from the soil or from the tree trunk. This will be carried out in a future study.

The application of Eqs. (1) and (4) requires values of the basal emission rates \( E_{i}^{\text{oak}} \) and \( E_{i}^{\text{pine}} \). We use \( E_{i}^{\text{oak}} \) values reported by Bertin et al. (1997) for sunny leaves \((0.85 \text{ µg m}^{-2} \text{ s}^{-1})\) and minimum values for completely shaded leaves \((0.05 \text{ µg m}^{-2} \text{ s}^{-1})\). According to these studies we use the basal emission as the reference value for leaves with a different physiological behavior for those being in shadow all the time and those being completely exposed to sunlight during the whole day. In between we estimate different basal emission rates \( E_{ij}^{\text{oak}} \) for each of the leaf angle classes \( i \) described by the radiation model. We simply assume a linear decrease of the reported \( E_{i}^{\text{oak}} \) values from 0.85 to 0.05 \( \text{µg m}^{-2} \text{ s}^{-1} \). In this study \( E_{i}^{\text{oak}} \) is, therefore, light dependent. For leaves in half shadow (e.g., Seufert et al. 1997) this results in a reduction of \( E_{i}^{\text{oak}} \) by 30% and therefore is comparable to the results from cuvette measurements. A further case study is also performed with constant values for \( E_{i}^{\text{oak}} \). For pines Staudt et al. (1997) report basal emission rates between 2.0 and 3.5 \( \mu \text{g g}^{-1} \text{ h}^{-1} \) for spring and 7.0 and 15.0 \( \mu \text{g g}^{-1} \text{ h}^{-1} \) for summer. From other field measurements, values up to 20 \( \mu \text{g g}^{-1} \text{ h}^{-1} \) are reported (Owen and Hewitt 1997). For this first study we take a basal emission rate of \( E_{i}^{\text{pine}} = 3 \mu \text{g g}^{-1} \text{ h}^{-1} \), which gives a value of \( E_{i}^{\text{pine}} = 0.036 \mu \text{g m}^{-2} \text{ s}^{-1} \) in the proper units. No data are reported on different values of \( E_{i}^{\text{pine}} \) for sunny or shadow needles. Therefore \( E_{i}^{\text{pine}} \) is assumed to be independent of light, and the chosen \( E_{i}^{\text{pine}} \) value is taken to be constant for all canopy layers and all leaf angle classes. Values of \( \beta_i \) and \( \beta_j \) in Eqs. (1) and (4) are set to 0.124 and 0.09 \( \text{K}^{-1} \), respectively, according to the mean results from cuvette measurements (e.g., Seufert et al. 1997). The standard temperature \( T_0 \) is equal to 30°C.

b. Fluxes above canopy

The total monoterpenic flux \( F_{\text{VOC}} \) modeled at a reference level of \( h = 19 \) m above the ground surface is calculated as the weighted contribution of the fluxes of the two dominant species observed in the study area at Castelporziano: 51%–55% pines and 13%–15% oaks (Staudt et al. 1997; Lenz et al. 1997):

\[
F_{\text{VOC}}^{10m} = 0.15 F_{\text{VOC}}^{10m} + 0.55 F_{\text{VOC}}^{10m}\]

(13)

We suppose that VOC fluxes above the canopy are related to the canopy temperature \( T_c \) through a function of the form \( F(T_c) = F_s \exp[\beta_s(T_c - T_s)] \). The fluxes simulated for two model runs, case A and case B, will be compared to examine the dependence of VOC fluxes above the canopy on \( T_c \) and on the temperature exponent \( \beta_s \) on the canopy level. Note that the emission rate as determined for leaf or branch level is described by a similar formula [see Eqs. (3) and (4)]. The study will focus on possible reasons for different \( \beta \) values found during experimental studies on leaf and canopy levels.

Figure 2 shows diurnal cycles of the modeled canopy temperature \( T_c \) for case A and case B. This temperature is the modeled leaf temperature calculated with Eq. (9) and averaged over the upper three crown layers, as it would be approximately measured by an infrared radiometer thermometer positioned above the tree stand. Modeled canopy temperatures reach a maximum of 21.1°C (case A) and 30.6°C (case B) around 1330 LT. This corresponds to field conditions described by Schween et al. (1997a).

Modeled VOC fluxes calculated with Eq. (13) are shown in Fig. 3. For case A the maximum VOC flux is 0.063 \( \mu \text{g m}^{-2} \text{ s}^{-1} \) and for case B it is 0.176 \( \mu \text{g m}^{-2} \text{ s}^{-1} \). These model calculations with FLAME yield values of VOC fluxes that are smaller by 40% than those experimentally derived fluxes for similar canopy temperatures. Among others, these discrepancies are due to the fact that we have not described in detail the morphological and physiological characteristics of the vegetation (e.g., stomata parameters, optical properties of leaves, etc.). But we also consider that values of the basal emission rates, \( E_{i}^{\text{oak}}, E_{i}^{\text{pine}} \), play an important role.

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in the determination of VOC fluxes above the canopy. These effects will be presented in the next section.

Figures 4 and 5 show modeled VOC fluxes versus canopy temperature $T_c$. As a consequence of the hysteresis observed on the simulations, a difference is made between modeled morning (0700–1300 LT) and afternoon fluxes (1300–1900). The best-fit slope has been determined for each case. Derived $\beta_c$ values for the fluxes above the canopy shown in Table 2 are much larger than the temperature exponents $\beta_1$ and $\beta_2$ calculated from leaf or branch cuvette data for oaks and pines. Schween et al. (1997a) have also derived $\beta_c$ from the analysis of fluxes of VOC measured by micrometeorological techniques above the canopy and obtained values in the same order of magnitude as the ones found in this study. Thus we expect that such differences can be attributed to the hydrological status of the plant soil system and to the influence of turbulent mixing on the fluxes $F(T_c)$.

The hysteresis effects shown in Figs. 4 and 5 were also observed for modeled net radiation, $R_{net}$, as well as for sensible and latent heat fluxes, $H$ and $\lambda E$. During the BEMA field studies performed above the mixed forest during 1993 and 1994 such a behavior was often found for these micrometeorological quantities for conditions with moist soil in the root zone. During the morning hours the atmosphere and the energy fluxes, $H$ and $\lambda E$, are driven by the available energy, $R_{net}$, and the conditions in the atmospheric boundary layer, where air temperature $T_a$ and absolute humidity, $q_a$, are usually smaller than $T_c$ and the absolute humidity in the stomata, $q_s(T_c)$. These differences cause a significant increase of all fluxes until about noon. In the afternoon, if transpiration is not limited, fluxes during the BEMA-94 experiment and also from the model calculations show that the flow above the canopy becomes stable in terms of the gradient of potential temperature and flux Richardson number for all conditions with Bowen ratios (BR) $\leq 0.8$. In addition, heating of the ABL or advection of warm air causes $T_a \approx T_c$, and $H$ becomes small and then ultimately negative, although the latent heat flux $\lambda E$ still was significantly large, as $q_a < q_s(T_c)$. For similar values of the canopy temperature $T_c$ the transilient matrix elements $C_{mm}$ [Eq. (10)] are smaller in the afternoon than in the morning hours. This is because not only the driving force $\Delta T = T_c - T_a$ but also the contribution of the buoyancy term to the TKE production are small or even zero in the afternoon. This, at first, causes the decrease of $H$ and then the decrease of the flux $\lambda E$ at 19-m height even if the plants would be able to evaporate without limitation. Therefore, as vertical mixing starts to be limited, any other flux, like the

| Table 2. Derived values of the temperature exponent $\beta_c$. |
|---|---|
| **Morning** | **Afternoon** |
| Case A | $0.22 \pm 0.001$ K$^{-1}$ | $0.272 \pm 0.002$ K$^{-1}$ |
| Case B | $0.128 \pm 0.001$ K$^{-1}$ | $0.262 \pm 0.002$ K$^{-1}$ |
VOC flux measured above the canopy shows the hysteresis behavior, although the emission rate from leaves potentially would be larger if only $T_c$ is considered. If quantities are well mixed within the ABL, the vertical concentration gradients $[I_m - I_n]$ in Eq. (10) also become smaller during the afternoon than during time before noon. This effect also contributes to the smaller fluxes after 1330 LT. For the idealized studies carried out in this section, derived $\beta_c$ values are larger during the afternoon as a consequence of mixing processes and the vertical concentration gradients above the canopy.

### c. Sensitivity study

The basal emission rate $E_s$ can be considered to be the capacity for emission of specific VOCs under certain fixed conditions. As mentioned previously, it was observed that leaves growing in half shadow have basal emission rates lower than those growing in full sun (e.g., Seufert et al. 1997; Bertin et al. 1997; Staudt et al. 1997). Some studies on leaves growing in deep shadow showed $E_s$ values lower by more than an order of magnitude. For case A and case B in the previous section such a behavior was simulated in a way that a light-dependent basal emission rate was modeled for oaks.

If all leaves would have comparable values of $E_s$, the results should be different. We take the warmer day (case B) as the control case and use exactly the same set of input data for the four sensitivity studies (runs 1–4) presented in this section. Therefore, the predicted vertical profiles of mean meteorological variables as well as the modeled leaf temperature and radiation regime within the canopy are the same for the control case B and for the other model studies.

In run 1 we consider the basal emission rate from oaks to be independent of light. We assume a unique constant value of $E_{s,\text{oak}} = 0.50 \mu g m^{-2} s^{-1}$ for all angle-oak classes and all canopy layers. The $E_{\text{pine}}$ value is the same used for control case B.

In run 2 we test the influence of a higher $E_{s,\text{pine}}$ value on the modeled VOC fluxes. We assume a basal emission rate for pines of $E_{s,\text{pine}} = 10 \mu g h^{-1} g^{-1}$, as given by Staudt et al. (1997) for summer conditions, which gives a value of $E_{\text{pine},\text{night}} = 0.121 \mu g m^{-2} s^{-1}$ in the proper units. For oaks we keep the light dependence of $E_{s,\text{oak}}$ as in the control case B.

Run 3 and run 4 show the results of a somewhat simplified form of the previous studies. Run 3 and run 4 are carried out assuming that the emission from oaks and pines [Eqs. (1) and (4)] are independent of the detailed nonlinear light regime within each canopy layer. This means that we do not apply the angle-dependent values of $T_{\text{leaf},ij}$ and PAR$_{ij}$ for the different leaf angle classes $i$, but we make use of the layer-averaged values $T_{\text{leaf},j}$ and PAR, in Eqs. (1) and (4). In run 3 we test again the use of a constant basal emission rate for oaks, $E_{s,\text{oak}} = 0.50 \mu g m^{-2} s^{-1}$, and keep $E_{\text{pine}}$ as in case B.

In run 4 we apply constant values of $E_{s,\text{oak}} = 0.50 \mu g m^{-2} s^{-1}$ and $E_{s,\text{pine}} = 0.121 \mu g m^{-2} s^{-1}$ for all layers within the canopy. Values of basal emission rate applied for these two studies are in the the range of those reported by Bertin et al. (1997) and Staudt et al. (1997).

Results of the modeled VOC fluxes using Eq. (13) are presented in Fig. 6 for all four case studies. In Table...
The one-dimensional Forest–Land–Atmosphere Model (FLAME) has been used to model the fundamental behavior of the diurnal cycle of VOC fluxes above an idealized 12-m-tall forest on a late spring day under cloud-free sky conditions. The simulations are performed with initial conditions and characteristics comparable to the conditions during the BEMA field phases 1993 and 1994 (e.g., Seufert et al. 1997; Schween et al. 1997a, b).

We examined the modeled VOC fluxes for two case studies, A and B, for which the modeled canopy temperature \( T_c \) reaches a maximum of approximately 21° and 31°C, respectively. We assumed that modeled VOC fluxes at a reference level above the canopy are related to \( T_c \) through a function of the form \( F(T_c) = F_s \exp[\beta_s(T_c - T)] \). From this equation we derived the temperature exponent \( \beta_s \) by deriving best-fit slopes. As a consequence of the hysteresis observed on the modeled fluxes, we made a distinction between morning (0700–1300 LT) and afternoon (1300–1900 LT) slopes. The mean \( \beta_s \) values obtained are \( \beta_s = 0.126 \pm 0.001 \) K⁻¹ for the morning VOC fluxes, and \( \beta_s = 0.267 \pm 0.002 \) K⁻¹ for the afternoon. These values are larger than those \( \beta_1 \) and \( \beta_2 \) derived at leaf scale from cuvette data.

A sensitivity study was conducted to show the importance of the basal emission rate, \( E_b \), on the total VOC fluxes above the canopy. Changes of \( E_b \) within the range of field observations produced modeled VOC fluxes more than two times larger than the values obtained for a reference case. Therefore, the accuracy of \( E_b \) seems to be very important for the determination of VOC fluxes when using FLAME or other models to calculate VOC fluxes to the atmosphere.

The hysteresis shown by the simulated VOC fluxes when plotted against \( T_c \) is also observed for the fluxes of sensible and latent heat and net radiation. This is

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**Table 3.** Modeled VOC fluxes (\( \mu g \, m^{-2} \, s^{-1} \)) for different canopy temperatures \( T_c \) during morning and noon.

<table>
<thead>
<tr>
<th>( T_c ) (°C)</th>
<th>24°C</th>
<th>25°C</th>
<th>26°C</th>
<th>27°C</th>
<th>28°C</th>
<th>29°C</th>
<th>30°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case B</td>
<td>0.0756</td>
<td>0.0885</td>
<td>0.1018</td>
<td>0.1160</td>
<td>0.1332</td>
<td>0.1512</td>
<td>0.1714</td>
</tr>
<tr>
<td>Run 1</td>
<td>0.0761</td>
<td>0.0991</td>
<td>0.1146</td>
<td>0.1327</td>
<td>0.1546</td>
<td>0.1799</td>
<td>0.2032</td>
</tr>
<tr>
<td>Run 2</td>
<td>0.1650</td>
<td>0.2120</td>
<td>0.2340</td>
<td>0.2578</td>
<td>0.2892</td>
<td>0.3231</td>
<td>0.3577</td>
</tr>
<tr>
<td>Run 3</td>
<td>0.0979</td>
<td>0.1310</td>
<td>0.1580</td>
<td>0.1895</td>
<td>0.2283</td>
<td>0.2704</td>
<td>0.3101</td>
</tr>
<tr>
<td>Run 4</td>
<td>0.2161</td>
<td>0.2537</td>
<td>0.2901</td>
<td>0.3321</td>
<td>0.3832</td>
<td>0.4385</td>
<td>0.4950</td>
</tr>
</tbody>
</table>

**Table 4.** Derived values of the temperature exponent \( \beta_s \).

<table>
<thead>
<tr>
<th></th>
<th>Morning ( \beta_s ) (K⁻¹)</th>
<th>Afternoon ( \beta_s ) (K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case B</td>
<td>0.128 ± 0.001</td>
<td>0.262 ± 0.002</td>
</tr>
<tr>
<td>Run 1</td>
<td>0.142 ± 0.001</td>
<td>0.281 ± 0.002</td>
</tr>
<tr>
<td>Run 2</td>
<td>0.110 ± 0.001</td>
<td>0.215 ± 0.002</td>
</tr>
<tr>
<td>Run 3</td>
<td>0.163 ± 0.002</td>
<td>0.339 ± 0.002</td>
</tr>
<tr>
<td>Run 4</td>
<td>0.133 ± 0.001</td>
<td>0.254 ± 0.002</td>
</tr>
</tbody>
</table>
caused by the interactions within the diurnal courses of the energy balances of the atmospheric boundary layer. The diurnal heating causes an early decrease of the sensible heat flux and therefore a stabilizaiton of the layer above a forest with well-watered soil in the root zone. When vertical mixing becomes limited in the early afternoon, the vertical concentration profiles are nearly constant with height and the net VOC fluxes for the same surface temperature become smaller than during the morning hours. This results in larger temperature coefficients $\beta$, compared to $\beta$ values from measurements on the leaf scale. Therefore, drier soil conditions or advection of dry or humid air, which changes not only the net radiation and $T_{\ast}$, but also the mixing conditions within the ABL, can also lead to this behavior. But these results also point toward a general influence of regional hydrologic conditions on the source strength of biogenic compounds and also of chemical conditions for oxidant formation.

Acknowledgments. We gratefully acknowledge the Commission of European Communities for supporting part of the model development and the German Ministry of Research and Development for the financial support of this study in the frame of the Tropospheric Research Program of the German Ministry of Research and Development.

REFERENCES


