Inferring the source strength of isoprene from ambient concentrations

Abhishek Tiwary a,*, José D. Fuentes b, Jordan G. Barr b, Daniel Wang c, Jeremy J. Colls a

a Agricultural and Environmental Sciences Division, School of Biosciences, The University of Nottingham, University Park, Nottingham, NG7 2RD, UK
b Department of Environmental Sciences, University of Virginia, Charlottesville, VA, USA
c Environmental Technology Center, Environment Canada, Ottawa, Ontario, Canada

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Abstract

This paper reports on the application of an inverse Lagrangian technique that uses localized near-field (LNF) theory to calculate the source strength profile of isoprene from deciduous forest canopies. The basic tenet considered in this study is that the prevailing ambient isoprene concentrations observed over forests represent the source strength of the underlying surface as the scalar is transported from the sites of biosynthesis to the measurement point above forest canopies. Using information on the distribution of active isoprene biomass and the plant canopy environment, a two-storey canopy model was developed and applied to estimate isoprene emission rate profiles for a monoculture aspen forest whose isoprene source is homogeneously distributed throughout the landscape. Modelled results show that isoprene emission rates strongly vary with canopy depth, with maximum values coinciding with canopy layers with largest amount of active biomass. The model also captures the strong diurnal patterns of isoprene emissions from the forest canopy. We conclude that the present modelling system provides a practical method for estimating isoprene emission rate profiles based on the knowledge of atmospheric turbulence and ambient concentrations.

Keywords: Isoprene; Source strength; LNF; Inverse Lagrangian model; Emission rate; Secondary organic aerosols

1. Introduction

Plants, particularly tree species, release substantial amounts of non-methane biogenic volatile organic compounds (BVOCs) including isoprene (C5H8), monoterpenes (C10H18), sesquiterpenes (C15H28), and oxygenated compounds (CnH2n-2O). Isoprene is the most abundantly emitted BVOC to the atmosphere by forests (Fuentes et al., 2000; Kesselmeier and Staudt, 1999). Due to the high ambient mixing ratios (e.g., 10–30 parts per billion on a volume basis, ppbv) and high reactivity with the hydroxyl radical (HO), in environments rich in nitrogen oxides and under favourable atmospheric conditions (i.e., plenty of sunlight) isoprene can contribute to the production of oxidants such as ozone (O3) (Cardelino and Chameides, 2000) and secondary organic aerosols (SOAs) (Seinfeld and Pandis, 1998). Laboratory-based studies also indicate that acid-catalysed multiphase reactions of isoprene produce oligomeric humic-like materials resulting in substantial aerosol formation (Iinuma et al., 2004; Limbeck et al., 2003). Improved estimates of isoprene emissions from terrestrial vegetation are still necessary to quantify the aerosol formation from isoprene via condensed phase reactions with hydrogen peroxide (Claeys et al., 2004). Knowledge of aerosol sources and distribution patterns is necessary to investigate the impacts of aerosols on the Earth’s climate and cloud formation processes.

The current understanding of the biochemistry and ecology of isoprene production and emission allows the integration of these processes from the scale of cells to the plant communities (Baldocchi et al., 1999; Fuentes et al., 1999). The integration of isoprene emissions from single foliage elements to the ecosystem level is normally achieved by the coupling of active biomass distribution, environmental conditions influencing emissions, and basal emission rates (Eb). A prerequisite of
this approach is to provide a priori basal emission rates and their variations with plant canopy depth (Geron et al., 1997). Model-based biogenic hydrocarbon estimates apply the emission algorithm proposed by Guenther et al. (1993), which uses experimentally-determined \( E_s \) values. This approach has been widely applied in estimating short-term variations of isoprene emissions for several plant species (Harley et al., 1997; Kesselmeier and Staudt, 1999). An alternative process-based approach, called the seasonal isoprene synthase model-biochemical isoprenoid biosynthesis model (SIM-BIM), relates isoprene emissions to the leaf-level isoprene synthase activity (Zimmer et al., 2003). Compared to earlier modelled emissions (e.g., Guenther et al., 1993), isoprene emissions derived with SIM-BIM correlate more favourably with measurements. The SIM-BIM includes dynamic emission rates, adjusted by modulating the enzymatic activities in accordance with the historical environmental conditions. However, the SIM-BIM requires detailed information on the biochemical properties of the enzyme involved in isoprene biosynthesis and on the activation of the isoprene enzyme (e.g., isoprene synthase) on both temperature and light levels. An alternative, practical method for determining isoprene basal emission rates is still necessary. Therefore, the goal of this study is to infer the vertical distribution of isoprene emission rates from ambient concentration gradients, employing an inverse Lagrangian technique (ILT) based on the localized near-field (LNF) theory (Raupach, 1989a,b). This goal is achieved by developing and applying a multi-layered canopy model for a monospecific aspen forest ecosystem whose isoprene source is homogeneously distributed throughout the landscape. We conclude that the present modelling system provides an alternative method for estimating isoprene emission rates based on the knowledge of atmospheric turbulence and ambient concentrations.

2. Field methods

The data sets to test the models described below (see Sections 3 and 4) came from the BOREAS field measurement program conducted during the growing season of 1994 (Sellers et al., 1995). Micrometeorology and isoprene data were obtained at Prince Albert National Park, Saskatchewan, Canada. This field site is situated in the southern boreal forest of Canada (53°36′N, 106°20′W). The forest consists of trembling aspen (Populus tremuloides), an effective isoprene emitter (Gu et al., 1999). Randomly situated throughout the 1994 growing season (see Black et al., 1996; Fuentes et al., 1999 for additional details). The forest canopy features an open trunk space between 2.5 and 15 m without foliage, and aspen leaves were distributed in the layer between 15 and 22 m above the ground. Between the ground and 2.5 m, a hazelnut (Corylus cornuta) under-storey with a LAI of 3.2 existed throughout the landscape. Cuvette measurements indicated that only the trees belonging to the Populus genus release isoprene.

Environmental conditions and flux measurements were determined within and above the forest canopy. Air temperature (12 levels), specific humidity...
(two levels above the forest), incoming solar radiation, incoming photosynthetically active radiation (PAR), and net radiation above the forest were continuously monitored throughout the growing season. Isoprene concentrations were determined from air samples taken simultaneously at seven levels (0.8, 6.0, 18.0, 27.0, 38.0, 60.0 and 100.0 m above the ground). The first five sampling intakes were mounted on the tower whereas the 60.0- and 100.0-m sampling intakes were installed on the line of a tethered balloon system. The tethered balloon remained at a fixed altitude throughout the sampling period. Air was drawn at fast flow rates (>20 L min$^{-1}$) through cleaned Teflon tubing. Teflon filters (2 mm diameter, 1-µm film thickness) of the gas chromatograph GC-FID were used to collect air samples at each sampling level. Atmospheric samples from the intakes were stored in electropolished canisters, which were evacuated at the beginning of each sampling period. Mass flow controllers regulated the constant flow rate (100–150 L min$^{-1}$) entering the canisters. Because isoprene is found in trace amounts in the air, the analyte required pre-concentration prior to its analyses. This was achieved by passing air samples through traps cooled at −150 °C. After thermal desorption at 120 °C, concentrated isoprene was introduced to the capillary column (model HP-1, 50 mm × 0.31 mm ID, 1-µm film thickness) of the gas chromatograph (GC-FID). All air samples were analysed within 24 h of air gathering. Details concerning GC-FID calibration and measurement accuracy can be found in Fuentes et al. (1996). Fig. 1 presents plots of height-resolved isoprene mixing ratios (in ppb) measured on 6 September 1994 between 0800 and 2000 h at Prince Albert National Park, Saskatchewan, Canada. Dashed lines denote canopy height.

3. Localized near-field (LNF) theory and its application to inverse Lagrangian technique

Under non-advective conditions the LNF theory offers a robust mechanism to predict the interaction between the within-canopy source- and sink-densities and the ambient concentration profiles (Gu et al., 1999; Katul et al., 1997; Nemitz et al., 2000; Raupach, 1989a,b; Siqueira et al., 2000). The essential premise is that the ensemble-averaged concentration, $C(z)$ of a scalar transported to a point at a height $z$ above the soil surface is the sum of both a persistence governed ‘near-field contribution’, $C_{nf}(z)$ and a diffusion governed ‘far-field contribution’, $C_{ff}(z)$ as follows:

$$C(z) = C_{nf}(z) + C_{ff}(z)$$  
(1)

with $C_{ff}(z)$ being described by the classical flux–gradient relationship, assuming an extensive horizontally homogenous and stationary medium.

$$F(z) = -K_{far}(z) \frac{\partial C_{ff}(z)}{\partial z}$$  
(2)

Here $F(z)$ is the within-canopy flux profile and $K_{far}(z)$ is the far-field turbulent eddy diffusivity, which is a function of $z$ and thermal stratification, expressed in terms of the Monin–Obukhov length ($L$). The integration of Eq. (2) between the limits $z$ and $z_r$ yields the following expression for the far-field contribution:

$$C_{ff}(z) = C_{ff}(z_r) + \int_{z_r}^{z} F(z) \frac{dz}{K_{far}(z)}$$  
(3)

Within the canopy $K_{far}(z)$ is modelled as:

$$K_{far}(z) = \sigma_w^2(z) T_L(z)$$  
(4)

and $F(z)$, which is height dependent, can be calculated as the integral over the source/sink layers as follows:

$$F(z) = F(\text{soil}) + \int_{0}^{z} S(z) dz$$  
(5)

Here $F(\text{soil})$ represents the scalar fluxes from soil and $S(z)$ is the source/sink distribution profile. The near-field concentration profile, $C_{nf}(z)$ is obtained as follows:

$$C_{nf}(z) = \int_{0}^{z} S(z_0) \sigma_w(z_0) \left\{ \frac{z - z_0}{\sigma_w(z_0) T_L(z_0)} \right\} \left\{ k_n \left\{ \frac{z + z_0}{\sigma_w(z_0) T_L(z_0)} \right\} \right\} dz_0$$  
(6)

The following expression for the non-diffusive ‘near-field’ contributions $k_n$ to the concentration of a variable $x$, derived by Raupach (1989a) (called as the ‘near-field kernel function’) has been considered applicable to estimate the $C_{nf}(z)$ profiles in earlier studies for conditions experiencing homogenous turbulence (Katul et al., 1997; Nemitz et al., 2000; Siqueira et al., 2000). Although for non-homogenous turbulence within the plant canopy, there has been reported departure of this parameterised diffusion cloud from the true near field (Gu, 1998; Katul et al., 1997).

$$k_n(x) = -0.39894 \ln(1-e^{-|x|}) - 0.15623 e^{-|x|}$$  
(7)

In the case of the inverse Lagrangian approach the measured concentration profile $C_i$ for $n$ layers ($i = 1, 2, \ldots, n$) and mean concentration at the reference height, $C_{ref}$ are used to estimate the source profile $S_i$ for $m$ source/sink layers ($j = 1, 2, \ldots, m$) by solving a system of $m$ linear equations. It is desired to have $n > m$ since the solution obtained in this way has been found to be sensitive to small errors in the
concentration measurements or the estimation of the standard deviation of the vertical wind speed $\sigma_w(z)$ and the Lagrangian time scale $T_1(z)$ (Raupach, 1989a). This results in the formulation of the following regression problem, where $S(z)$ is estimated by the least squares approach.

$$ \sum_{k=1}^{k=m} A_k S_k = B_j, \quad j = 1, \ldots, m \tag{8} $$

$$ A_k = \sum_{i=1}^{i=n} D_{ij} dz \Delta D_{ik} dz_k \tag{9} $$

$$ B_j = \sum_{i=1}^{i=n} (C_i - C_{ref}) D_{ij} dz_j $$

In Eq. (9), $D_{ij}$ represent the elements of the dispersion matrix, $C_i$ and $C_{ref}$ denote the scalar concentration at layer $i$ and reference level (see nomenclature table for symbol definition). In the case of small sample size (i.e., few profile concentration measurements) the above approach has limited effectiveness in smoothing the $S(z)$ profiles (Siqueira et al., 2000) and therefore the simulated source strengths between adjacent levels could still remain unrealistically large. In order to avoid this uncertainty, a priori information is needed about the source strength distribution within the canopy based on the weighted measures of length approach (Menke, 1989). This approach provides an additional smoothness constraint on Eqs. (8) and (9). Details of the adopted numerical formulation can be found in Siqueira et al. (2000).

4. Model implementation

4.1. Discretisation of the LNF problem

To predict the isoprene emission rate in the discrete layers of a vegetation canopy, $E_{is}(z)$ the original algorithm suggested by Guenther et al. (1993) has been re-arranged, as shown in Eq. (10). This formulation requires layer-wise information on the within-canopy source strength of the isoprene emitting biomass ($\Delta S_{Isoprene}(z)$), the leaf temperature ($T_{leaf}(z)$), photosynthetically active radiation (PAR($z$)), and the leaf area density (LAD($z$)) for each source layer (Fuentes et al., 1998).

$$ E_{is}(z) = \frac{\Delta S_{Isoprene}(z)}{LAD(z)f(PAR(z))f(T_{leaf}(z))} \tag{10} $$

In this paper, the inverse Lagrangian technique (ILT) has been applied to obtain $\Delta S_{Isoprene}(z)$ and $T_{leaf}(z)$ from the measured ambient isoprene concentrations and air temperature. The subsequent sections describe the algorithms applied to quantify the vertical distribution of velocity statistics, radiation fields and leaf photosynthetic parameters required to predict the source/sink densities.

For the purpose of this study, the implementation of LNF theory is achieved by defining Eqs. (3) and (6) into $m$ source/sink layers of distinct source strengths, $S_j$, with the top boundary of the uppermost source layer coinciding with the canopy height. The scalar concentration, $C_i$ is allocated at the centre of each layer $i$ at $n$ heights within the canopy. An additional concentration layer at the reference height just above the plant canopy, $C(z_{ref})$ had to be defined as well. Since the aspen canopy is assumed to remain horizontally homogeneous, a representative Gaussian distribution is applied to model the dispersion in homogenous steady turbulence following earlier studies (Katul et al., 1997; Warland and Thurtell, 2000). The source strengths and the concentrations are then related to each other by a two-dimensional dispersion matrix, $D_{ij}$, which describes the contribution of source layer $S_j$ to the concentration layer $C_i$ from Eq. (11):

$$ C_i - C(z_{ref}) = \sum_{j=1}^{j=m} D_{ij} S_j \Delta z_j + D_{C\text{G}} G $$

$D_{ij}$ is computed by considering a source density $S_j$ in layer $j$, and zero elsewhere for which $C_i$ is estimated in all layers using $C(z_{ref})$. This step is repeated for all the source layers using Eq. (12):

$$ D_{ij} = \frac{C_i - C(z_{ref})}{S_j \Delta z_j} $$

The $D_{C\text{G}}G$ term in Eq. (11) is the concentration contribution from soil, where $F_G$ is the soil flux. $D_{C\text{G}}$ is the dispersion matrix for the soil and is calculated from:

$$ D_{C\text{G}} = \int_{z_l-0.5\Delta z_l}^{z_{u}} \frac{1}{\sigma_w^2(z')T_L(z')dz'} + \frac{2}{\sigma_w(0)} \left[ \frac{z_l-0.5\Delta z_l}{\sigma_w(0)T_L(0)} \right] $$

In the simple case of $m = n$, the linear system described by Eq. (11) can be solved either for concentrations (“forward problem”) or source strengths (“inverse problem”). The former requires inputs of a number of micrometeorological variables obtained at the reference height. In addition, detailed information on the biophysical state of the canopy is necessary to predict the source strength a priori, which makes this technique more demanding in terms of the physiological inputs. It mainly takes into account the radiation transfer mechanism and the partitioning of leaf and air temperature within the vegetation canopy to estimate the emissions (hence in the present paper this model has been termed as EMISSION). On the other hand, the latter approach only requires information on the measured concentration values, $C(z)$ and turbulence information on the vertical velocity standard deviation, $\sigma_w$, and the Lagrangian integral timescale, $T_L$, to describe the diffusion of scalars within the plant canopy using inverse Lagrangian technique, ILT (hence this model has been termed as INVERSE).

The model described above was applied to estimate the source/sink distribution for isoprene, carbon dioxide, and heat. The carbon dioxide application was made to investigate
if the model provides reliable results which are compared to measurements. The source/sink distribution associated with the aspen–hazelnut canopy was divided into eight concentration measurement levels \( n \) and six source/sink layers \( m \) for estimating carbon dioxide and heat fluxes. Since field studies (Fuentes et al., 1996; Gu et al., 1999) suggest that only aspen foliage has the isoprene emitting biomass, a slightly different discretisation was applied for estimating the isoprene source strengths in which case the canopy was divided into six concentration measurement levels \( n \) and five source/sink layers restricted only between 15 and 22 m above the ground (Fig. 2). However, additional tests were performed with numerically interpolated layers in between the measured values to assess the influence of varying their values on the simulation outputs.

4.2. Estimation of within-canopy velocity statistics profiles

The model described above requires atmospheric turbulence data as input variables to Eqs. (4) and (6). In the absence of routine measurements for the entire sampling period the profiles of the standard deviation of the vertical wind velocity, \( \sigma_w(z) \) and the Lagrangian time scale, \( T_L(z) \) within and above the forest canopy are obtained by applying the one-dimensional, second-order closure model proposed by Massman and Weil (1999). The model uses the second-order closure scheme of Wilson and Shaw (1977) to determine canopy momentum transfer. The governing model equations are described in Eqs. (14) and (15):

\[
\frac{\sigma_w(z)}{u^*} = \nu \gamma_w \left[ \nu \gamma_w e^{-\chi(h)Q(z)} + B \left( e^{-3nQ(z)} - e^{-\chi(h)Q(z)} \right) \right]^{1/3}
\]

(14)

and

\[
\frac{T_L(z)u^*}{h} = \frac{L_w(z)}{\sigma_w(z)}
\]

\[
= 0.6 \left( 1 - \frac{d}{h} \right)^{1/2} \left( \frac{\sigma_w(z)}{u^* \gamma_w} \right)^{-1/2} \text{ for } z \leq h
\]

\[
= 0.6 \left( 1 - \frac{d}{h} \right)^{-1/2} \frac{(z - d)}{h} \text{ for } z \geq h
\]

(15)

Here \( L_w(z) \) is the within-canopy vertical Lagrangian length-scale, \( u^* \) is the friction velocity, \( d \) is the zero plane displacement height (taken here as 0.65 of canopy height) and \( \gamma_w \) is a model constant [quantified in terms of \( \sigma_w/u^* \) after Raupach et al. (1991)]. The proposed model uses a parameterisation of the within-canopy normalised \( T_L \) profile as a function of \( \sigma_w(z) \) profile instead of a height constant parameterisation suggested by Raupach (1989a) in order to account for the non-homogeneity in foliage distribution of the two-storey canopy. Details of the numerical expressions for the parameters involved are given in Appendix A.

This atmospheric turbulence model was adopted since the output profiles take into account the vertical canopy structure and the variation in the within-canopy foliage density. This has been an important consideration while defining the
discontinuous, bi-modal foliage distribution of the aspen—hazelnut stand (Fig. 3) owing to a wide trunk space region in between the hazelnut under-storey and the aspen over-storey. The within- and above-canopy formulations for the normalised $T_L(z)$ profile remain continuous at $z = h$. In addition, the approach accounts for the interference of neighbouring foliage elements within the canopy by introducing a momentum shelter factor.

Despite the sophisticated applicability of the Massman and Weil (1999) model, it has been reported to overestimate the stream-wise velocity attenuation within the canopy. In such circumstances, this would lead to lowering of the boundary layer heat conductances, both at the leaf-level and from the soil (see Eqs. (18) and (19)), thereby resulting in the overestimation of the modelled leaf temperature and potentially higher source strengths predicted from EMISSION in the deeper layers of the canopy. In order to minimise such anomalies, as a first step in this study, the outputs from the original model were compared with the locally measured profiles of $u^*$ (obtained at 37.4 m above the ground) for 26 July, 3–4 August, 6 and September 1994. The solid line represents values included in the model whereas the ● denotes measured data.

![Fig. 4. A comparison between the model output and measured profiles for the standard deviation of the vertical wind speed, $s_w(z)$, normalised to the friction velocity, $u^*$ (obtained at 37.4 m above the ground) for 26 July, 3–4 August, 6 and September 1994. The solid line represents values included in the model whereas the ● denotes measured data.](image)

### 4.3. Estimation of leaf temperature profile

The leaf temperature profile in the foliage layers, $T_{\text{leaf}}(z)$ for the entire aspen—hazelnut canopy is estimated from INVERSE. In the first step, the vertical profile of sensible heat sources, $S_h(z)$ is estimated using Eq. (11) with an input of the measured ambient air temperature data, $T_{\text{air,i}}$, ($i = 1$ to $n$) and an additional measurement taken at the reference height just above the canopy, $T_{\text{air,ref}}$. For the purpose of computing the dispersion matrices $D_h$ and $D_G$, the atmospheric turbulence statistics estimated in Section 4.2 are applied in the model. Thereafter, Eqs. (16) and (17) have been used to estimate the within-canopy leaf temperature profile $T_{\text{leaf}}(z)$ and the soil temperature, $T_{\text{soil}}$ from their respective heat sources:

$$S_h(z) = 2\rho_p c_p [T_{\text{leaf}}(z) - T_{\text{air}}(z)]$$  \hspace{1cm} (16)

$$S_G = 2\rho_p c_p (T_{\text{soil}} - T_{\text{air,i}})$$  \hspace{1cm} (17)

Here $\rho_p$ is the density of air, $c_p$ is the specific heat of air at constant pressure, $\theta_{\text{bl}}(z)$ is the profile of leaf boundary layer conductance to heat transfer, which is modelled after Sellers et al. (1996) from the vertical profiles of velocity, $u(z)$ and the leaf area density, LAD$(z)$, and is given by Eq. (18).

$$\theta_{\text{bl}}(z) = \frac{6.62 \times 10^{-3}}{2 (1 + \text{LAD}(z)^{0.6})} \left( \frac{u(z)}{d} \right)^{0.5}$$  \hspace{1cm} (18)

![Fig. 3. Leaf area density profile for the aspen—hazelnut forest canopy.](image)
and \( g_{bh0} \) is the conductance for heat from the soil to the centre of the lowermost canopy layer (i.e., the conductance for heat from the soil to the centre of the first layer in the model), which is derived from momentum transfer theory (Monteith and Unsworth, 1990) as shown in Eq. (19):

\[
g_{bh0} = \frac{k^2 u (0.5 \Delta z_1)}{\left( \ln \frac{0.5 \Delta z_1}{z_{os}} \right)^2} \tag{19}
\]

where \( z_{os} \) is the roughness length for momentum of the soil surface with representative value for the site as 0.01 m; \( \Delta z_1 \) is the thickness of the layer nearest to the ground.

The \( T_{leaf}(z) \) profile estimated above from INVERSE is solely dependent on its performance in estimating \( S(z) \) profiles directly from the measured ambient air temperature profile and the turbulence parameters and is therefore susceptible to measurement errors and to the noise introduced in turbulence modelling. Hence, as a crucial step, prior to its actual application in estimating isoprene source strength, the modelled \( T_{leaf}(z) \) profile was used to predict carbon dioxide concentration profiles from the formulation suggested in Section 4.5, which were validated against the measurements made between 1200 and 1300 h and between 1400 and 1500 h for 6 September 1994. This provided an independent assessment of the overall performance of EMISSION.

4.4. Estimation of profiles of photosynthetically active radiation for the aspen canopy

The PAR(z) profile is estimated using the two-stream radiative transfer model adopted from Sellers et al. (1996) with a transmission correction parameter added to account for the clumpiness arising from the grouping of foliage elements. This is achieved by introducing an “effective LAI”, which is the product of the actual LAI and a clumping index, to replace the actual LAI in the two-stream equations following Wang et al. (1997). Based on the measurements reported for the boreal aspen forest in Wang et al. (1997), a clumping index of 0.7 has been used. The leaf orientation distribution of the canopy is described by an ellipsoidal function (Campbell and Norman, 1989, 1998), which has been considered suitable to model any natural canopy having a unimodal leaf angle distribution with the mean leaf angle ranging between 9° and 88° (Gu, 1998).

In addition, the isotropic scattering assumption in the original model is also replaced by a bi-Lambertian leaf scattering model to account for realistic canopy reflectance and transmission regimes. In this case, the incident solar radiation is partitioned into four components: direct PAR, diffuse PAR, direct near infrared radiation (NIR) and diffuse NIR by using the relations described in Spitters et al. (1986). This revised two-stream model has already been tested against measurements of canopy reflectance from an aspen forest and transmission from a mixed deciduous forest (Gu, 1998).

4.5. Estimation of the source/sink distribution and canopy fluxes of carbon dioxide from EMISSION

In this study, the source/sink distribution and canopy fluxes of carbon dioxide are modelled to ascertain whether the modelling system can realistically capture the turbulent exchanges of trace gases. Thus, the \( S(z) \) profiles for carbon dioxide were obtained using the biochemical model of photosynthesis (Farquhar et al., 1980; Woodward et al., 1995) as in Eq. (20).

\[
S_c = \min \{ W_c, W_j, W_p \} \left( 1 - \frac{0.5 P_O}{\tau C_{pp}} \right) - R_d \tag{20}
\]

Here \( S_c \) is the source density of carbon dioxide (in \( \mu \text{mol} \text{CO}_2 \text{m}^{-2} \text{s}^{-1} \)) and \( W_c, W_j \) and \( W_p \) represent the rate of carboxylation limited solely by the amount, kinetic properties and activation state of ribulose bisphosphate carboxylase–oxygenase (Rubisco); the rate of carboxylation controlled solely by the rate of RuBP regeneration in the Calvin cycle; the rate of carboxylation controlled by triose phosphate utilization, respectively (all in \( \mu \text{mol} \text{CO}_2 \text{m}^{-2} \text{s}^{-1} \)). The \( \tau \) is the specificity factor (dimensionless) of Rubisco for carbon dioxide relative to molecular oxygen, \( C_{pp} \) and \( P_O \) are the intercellular carbon
dioxide partial pressure and the internal partial pressure of oxygen (both in Pa) and \( R_d \) is non-photorespiratory respiration. Here \( C_{tp} \) was calculated by solving a system of three nonlinear equations according to the steps described in Gu et al. (1999). Appendix D of the same work details the soil and stem respiration models used to determine the \( CO_2 \) partial pressure profiles in this study. Layer-wise leaf-to-canopy integration of \( S(z) \) obtained from Eq. (21) is used to estimate canopy level carbon dioxide fluxes, \( F_c(z) \) as follows:

\[
F_c(z) = F(0) + \int_{z_1}^{z_2} S(z)dz
\]

where \( z_1 \) is the lowermost and \( z_2 \) is the uppermost layer of the scalar source. In the case of carbon dioxide, these values ranged between 0–2 m and 15–22 m covering emissions from soil, hazelnut under-storey and the aspen over-storey.

4.6. Application of inverse Lagrangian model (INVERSE) to estimate canopy fluxes

The inverse Lagrangian technique based on LNF theory has been implemented by earlier investigators to estimate fluxes of carbon dioxide and sensible heat from measured concentration profiles for forest canopies (Katul et al., 1997; Siqueira et al., 2002, 2000) and ammonia for an oilseed rape canopy (Nemitz et al., 2000). Very recently, its application to estimate the fluxes of biogenic hydrocarbons has been reported (Karl et al., 2005, 2004). In the proposed model, the source layers for isoprene have been restricted to canopy heights between 15 and 22 m since only aspen foliage released isoprene. However, in case of carbon dioxide the source layers were adjusted to account for carbon dioxide fluxes from the soil and the hazelnut under-storey as well. No a priori information was introduced while estimating isoprene fluxes since the source layers have been considered to remain continuous in the aspen canopy. However, in the case of carbon dioxide a source layer profile rising up to 2 m from the ground was used to account for fluxes from the soil and the hazelnut stand. Then a single source was used between 2 and 15 m with a priori information of source strength to be zero to simulate the contribution of the trunk space. Following this approach, a finer grid was used to locate the \( S(z) \) profiles in the aspen canopy.

Likelihood of uncertainties occurring due to the small number of source layers has been minimised by applying finer computation grid spacing. This also improved the resolution of estimates of \( \sigma_w \) and \( T_i \) profiles, which bear strong height dependence. In the first instance variable grid spacing for the computational domain, in case of both carbon dioxide and isoprene, were applied following Katul et al. (1997) p. 9315 to test the sensitivity of grid spacing on the smoothness of the resulting \( S(z) \) profiles. For this purpose, three different grid sizes, \( dz = 1 \) m, 0.5 m, and 0.25 m, were used. The resulting profiles for isoprene have been presented below (see Section 5.2). It was found that the smallest grid spacing produced the most resolved profile, and therefore, in order to minimise the noise in the estimated profiles, we implemented the finest grid spacing in all subsequent simulations. However, Katul et al. (1997) recommends that \( dz < 0.001 \) m (also known as “the Kolmogorov micro-scale”) should be avoided as it leads to generation of a large number of simultaneous equations whose solution is susceptible to numerical instabilities resulting from the Gauss–Jordan elimination method for inverting matrices (Press et al., 1996).

Following Eqs. (5) and (21), the canopy level fluxes of carbon dioxide, \( F_{canopy} \), have been obtained by integrating the source strengths for discrete layers, shown in Eq. (22).

\[
F_{canopy} = F_0 + \sum_{z=1}^{z=m} \Delta S(z)\Delta z
\]

where \( 1, \ldots, m \) are the discrete source layers and \( F_0 \) is the flux from the ground. In the case of isoprene \( F_0 \) is set to zero. It is important to note that unlike compensation point models required for estimating fluxes of several other compounds, the description of transport in the current model has very little effect on the resulting fluxes. It was assumed that all isoprene emitted by the vegetation exit the model domain and there was no feedback on concentrations after emissions.

5. Results and discussion

5.1. Source strengths and fluxes of \( CO_2 \) obtained from EMISSION and INVERSE

Since isoprene is a short-lived scalar, undergoing rapid depletion in its concentration, in the first step, the efficiency of INVERSE in estimating the \( S(z) \) profiles from measured \( C(z) \) profiles was tested for carbon dioxide, with common parameterisation of canopy turbulence structure as subsequently used for isoprene in Section 5.2. However, the source/sink layers in this case were appropriately adjusted to account for carbon dioxide fluxes from the ground and the hazelnut under-storey (Section 4.1).

Plots for ensemble-averaged carbon dioxide fluxes obtained for sampling done during days of year (DOY) 207, 215, 216 and 249 are presented, along with one standard deviation of the measured values, in Fig. 6. In the initial phase, all model runs were performed assuming near-neutral stability conditions. Carbon dioxide fluxes obtained from EMISSION have a smoother diurnal variation compared to the corresponding results obtained with the INVERSE method. This could be explained by the fact that the former is estimated from forcing variables (e.g., incident radiation) having small temporal variation, whereas the latter is subjected to measurement errors in the mean concentrations. However, application of an hourly ensemble-averaging period appears to have reduced the noise compared to the 30-min averaging period used by Siqueira et al. (2002). There is a better agreement between the nighttime carbon dioxide fluxes predicted from EMISSION and those derived from observed values (termed here as MICROMET) compared to the corresponding day-time fluxes. This pattern resembles earlier results reported for the same canopy (see Fig. 2 p. 890 of Baldocchi et al. (1999)). Also,
the night-time fluxes from EMISSION remain lower than INVERSE for the corresponding hours, with INVERSE overestimating the fluxes derived from MICROMET during this time of the day. Siqueira et al. (2002) attributes this to the ability of inverse models in capturing the carbon dioxide build up in the lower canopy layers resulting in large concentration gradients, thereby leading to enhancement of the corresponding source strengths. Lai et al. (2002), Leuning (2000) and Siqueira et al. (2002) associate additional discrepancy with the limitations of the neutral stability assumption while modelling the nocturnal $\sigma_w(z)$ and $T_1(z)$ profiles. This is because in the general budget equations the buoyancy production term is dependent upon atmospheric stability (Leclerc et al., 1990), which is overlooked while restricting the calculation of the velocity statistics with the neutral stability criteria. In such circumstances, the $D_{ij}$ is likely to be underestimated for stable, nocturnal conditions, thereby leading to the overestimation of fluxes from INVERSE. As the turbulence length and time scales for $z/h < 0.25$ are found to be influenced mainly by the presence of the lower surfaces and stability effects are minimal (Leuning, 2000) the overall canopy fluxes are assumed to fluctuate under varying stability conditions only in the height range $0.25 < z/h < 2.5$.

As a next step, in this study the influence of atmospheric stability on the predicted canopy level carbon dioxide fluxes was assessed by correcting the flow statistics and re-computing the day-time and the night-time fluxes separately for the corresponding sampling days. For this purpose the Monin–Obukhov similarity theory (Kaimal and Finnigan, 1994) was applied and the method described in Leuning (2000) was followed to account for the stability effects on the $\sigma_w(z)$ and $T_1(z)$ profiles for $z/L > 0$ at the canopy top ($L$ being the Obukhov length). The sampling days were split into day-time and night-time intervals and the velocity statistics for the night-time hours were adjusted assuming stable conditions while the corresponding variable for the day-time hours were calculated assuming neutral conditions. The adjusted $\sigma_w(z)$ and $T_1(z)$ profiles were then used to re-compute the canopy fluxes for the day-time and night-time hours separately. Following this, the revised predicted canopy fluxes from both EMISSION and INVERSE were compared with the estimated MICROMET values from eddy covariance measurements for the corresponding hours in terms of the statistical parameters shown in Table 1. In general, the fluxes predicted from EMISSION seem to have better agreement with MICROMET compared to INVERSE under all conditions, especially for the day-time simulations. However, the level of agreement between the predictions and the estimated values increased when the day-time and night-time fluxes were computed separately. Specifically, the fluxes output from INVERSE for the day-time and night-time hours showed much higher correlation with MICROMET data compared to the corresponding overall predictions assuming neutral-stability at all times of the day (respective $R$ values being 0.57, 0.43 and 0.34). This suggests that appropriate parameterisation of stability effects to adjust the modelled profiles of the standard deviation of vertical velocity and the Lagrangian time scale enhance the predictive power of the INVERSE model for night-time hours. Although adequate representation of night-time fluxes resulted in better agreement between the modelled and the measured canopy fluxes for carbon dioxide, the practical implication of extending this approach to predicting isoprene fluxes was considered futile assuming isoprene release to be a direct function of PAR.

5.2. Source strengths of isoprene obtained from INVERSE

Having established the reliability of the model formulation for forest–atmosphere carbon dioxide exchange, the application of INVERSE was extended to obtain the source strength profiles of isoprene, $S_{\text{isoprene}}(z)$ from their measured concentration profiles for 6 September 1994. In the first instance, the influence of grid resolution on the output source strength profiles was tested by using three grid sizes, as described above (see Table 1).

<table>
<thead>
<tr>
<th></th>
<th>Day-time</th>
<th>Night-time</th>
<th>Overall</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Slope</td>
<td>Intercept</td>
<td>RMSE</td>
</tr>
<tr>
<td>EMISSION</td>
<td>0.63</td>
<td>-0.07</td>
<td>0.32</td>
</tr>
<tr>
<td>INVERSE</td>
<td>1.12</td>
<td>0.37</td>
<td>0.71</td>
</tr>
</tbody>
</table>

The correlation coefficient ($R$) and the root-mean squared error (RMSE in $\mu$mol m$^{-2}$ s$^{-1}$) show the level of agreement between the measured and the predicted fluxes for the two models. (Note: each comparison involved 192 data points obtained from 30-min ensembled averaged fluxes for the sampling DOY 207, 215, 216 and 249).
Section 4.6). A much smoother $S_{\text{isoprene}(z)}$ profile was obtained using $dz = 1$ m, with the maximum predicted source strength lying within 0.1 nmol m$^{-3}$ s$^{-1}$. On the other hand, increasing the resolution of the grid from 1 to 0.5 m slightly improved the source profiles, whereas, grid spacing of 0.25 m provided a better resolved $S_{\text{isoprene}(z)}$ profile, peaking around 0.25 nmol m$^{-3}$ s$^{-1}$ and 0.35 nmol m$^{-3}$ s$^{-1}$, respectively (Fig. 7). Nevertheless, in all these cases the profiles peaked in the region between 50 and 75% of the aspen canopy, corresponding to the zone of densely populated aspen leaves. This correlated well with the vertical distribution of the potential isoprene active biomass. Aspen trees present at the sampling site are characterised by trembling leaves (hence also called “tembling aspen”). This allowed penetration of the incoming solar irradiance into their deeper layers, thereby increasing the concentration of the photosynthetic photon flux density which triggered the isoprene emissions in their central regions. Unfortunately, the conventional algorithm used in estimating isoprene emission rate from leaves only utilises normalised functions of specified leaf temperature and photon flux density. The emission factor used in such algorithms is not designed to account for subtle effects of leaf fluttering, which may be altering the radiation regimes in the inner canopy layers quite drastically. The direct estimation of isoprene source strength from measured concentrations appears to account for these effects.

5.3. Estimation of isoprene emission rates profiles

Vertical profiles of isoprene emission rates, $E_s(z)$ were estimated only for the period 0700–1800 h considering this time scale to adequately represent the modelled isoprene activity at the measurement site. The $E_s(z)$ profile obtained for 1200–1300 h (Fig. 8) indicates that the largest values coincide with the level of maximum foliage density. It is noteworthy that $E_s$ in most of the layers in the upper regions during the 1-h period remained above 15 nmol m$^{-2}$ s$^{-1}$. However, $E_s$ values estimated for the lower canopy regions remained much smaller. This result shows the capability of INVERSE in estimating dynamic time-dependent $E_s$ profiles. A contour plot of the $E_s$ profiles estimated using INVERSE from the ensemble averaged $S(z)$ profiles between 0700 and 1800 h (Fig. 9) shows that $E_s$ in the upper canopy layers remain above 15 nmol m$^{-2}$ s$^{-1}$ during most of the daylight hours. The relatively high $E_s$ values in the upper aspen canopy are strongly influenced by high PAR values and foliage temperature.

6. Summary and conclusions

A two-storey canopy model was developed and applied to estimate isoprene emission rate profiles for a monoculture aspen forest whose isoprene source is homogeneously distributed throughout the landscape. To apply the model, it is required to provide information on active biomass (e.g., vertical leaf area distribution), ambient isoprene concentrations, and atmospheric conditions (e.g., photosynthetically active radiation, air temperature and atmospheric turbulence) above the forest canopy. When applied to an aspen forest canopy the model captured the strong vertical variations in isoprene emission rates, with maximum values coinciding with canopy layers with largest amount of active biomass. The model also reproduced the strong diurnal patterns of isoprene emissions from the forest canopy. In the current model formulation, the effects of chemical processing of isoprene within the forest canopy were not considered. For dense forest canopies under the influence of high levels of free radicals (e.g., hydroxyl radical) and nitrogen oxides it is necessary to include the effects of chemistry as air parcels may experience sufficiently long residence times (i.e., >10 min) within the canopy for concentration gradients to be modified by the chemical reactions. Additional model tests need to be performed for forest canopies whose isoprene source is heterogeneously distributed across

![Fig. 7. Time-averaged within-canopy isoprene source/sink distribution ($S_{\text{isoprene}(z)}$) over model runtime period between 1200 and 1300 h for 6 September 1994 from INVERSE plotted as a function of height for a monoculture aspen canopy using three computational grid layer $dz = 0.25$ m, 0.5 m and 0.75 m, respectively.](image1)

![Fig. 8. Vertical profile of within-canopy isoprene emission rates, $E_s$ averaged over a period of 1200–1300 h on 6 September 1994.](image2)
the landscape. This might represent a challenging task as not all tree species release isoprene. And even the emitting plant species exhibit a great deal of variability in the isoprene emissions rates. Nonetheless, the main conclusion of this study is that the present modelling system provides a practical method for estimating isoprene emission rate profiles for monoculture vegetation based on knowledge of atmospheric conditions and ambient trace gas concentrations.

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Appendix A. Canopy momentum transfer and turbulence model

This model estimates the normalised within-canopy horizontal wind speed profile, $u(z)/u(h)$, assuming $u(z)$ to be a function of the cumulative leaf drag area per unit planform area, $\zeta(z)$ after Massman (1997) as follows:

$$\frac{u(z)}{u(h)} = e^{-n[1-\zeta(z)/\zeta(h)]}$$

(A1)

Here,

$$\zeta(z) = \int_0^z \frac{C_d(z')u(z')}{P_m(z')} \, dz'$$

(A2)

where $C_d$ is the drag coefficient of the foliage elements; $c_1$, $c_2$ and $c_3$ are the model constants related to the bulk surface drag coefficient $(=2u^2/\nu h^2)$ and to the substrate or soil drag coefficient obtained by Massman (1997). The original values of these constants used in the Massman (1997) model and the adjusted values used in the present study are shown in Table 1A. These adjustments have been made mainly to account for the discrepancy in the model predictions owing to the inadequate parameterisation of the constants used to define $u_*/u(h)$ according to the recommendations made by Massman (1997) (pp. 410—411 and his Fig. 1). Outputs from the above momentum transfer model form input to the analytical canopy turbulence model of Massman and Weil (1999) to obtain $\sigma_w$ and $T_i$ described in Section 4.2. Basic assumptions are that the within-canopy velocity variances ($\sigma_u^2, \sigma_v^2, \sigma_w^2$) remain proportional to the turbulent kinetic energy, $\sigma_e^2 = 1/2(\sigma_u^2 + \sigma_v^2 + \sigma_w^2)$. The input parameters used in the main turbulence model have been computed as follows:

$$Q(z) = \frac{1 - \zeta(z)}{\zeta(h)}$$

(A7)

$$B_1 = \frac{-(9/2)[u_*/u(h)]}{\alpha \nu_1 \{ (9/4) - A^2 u_*/u(h) \} }$$

(A8)

$$A = \frac{\sqrt{3} \nu_1}{\alpha}$$

where $\alpha = 0.05$; $\nu_1 = (\gamma_u^2 + \gamma_v^2 + \gamma_w^2)^{-1/2}$ and $\nu_3 = (\gamma_u^2 + \gamma_v^2 + \gamma_w^2)^{1/2}$.

Here $\gamma_i = c_i/u_*$ at and above the canopy ($i = u, v, w$) giving $\gamma_u = 2.4$, $\gamma_v = 1.9$, and $\gamma_w = 1.25$ as suggested by Raupach et al. (1991).

Table 1A

<table>
<thead>
<tr>
<th></th>
<th>$c_1$</th>
<th>$c_2$</th>
<th>$c_3$</th>
<th>$C_d$</th>
</tr>
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<tr>
<td>Present study</td>
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<td>0.264</td>
<td>15.1</td>
<td>0.2</td>
</tr>
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</table>

Fig. 9. Contour plot of $E_s$ profiles estimated from INVERSE using the ensemble-averaged isoprene source strength, for 0700—1800 h on 6 September 1994. The contours are expressed in units of nanomoles per metre square per second (nmol m$^{-2}$ s$^{-1}$).
References


