

Effects of surface conditions, dynamics and chemistry on SOA-evolution

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Combined effects of surface conditions, boundary layer dynamics and chemistry on diurnal SOA-evolution

R. H. H. Janssen¹, J. Vilà-Guerau de Arellano², L. N. Ganzeveld¹, P. Kabat^{1,*}, J. L. Jimenez³, D. K. Farmer⁴, C. C. van Heerwaarden⁵, and I. Mammarella⁶

¹Earth System Science and Climate Change, Wageningen University and Research Centre, Wageningen, The Netherlands

²Meteorology and Air Quality Section, Wageningen University and Research Centre, Wageningen, The Netherlands

³CIRES and Department of Chemistry and Biochemistry, University of Colorado, Boulder, CO, USA

⁴Department of Chemistry, Colorado State University, Fort Collins, CO, USA

⁵Max Planck Institute for Meteorology, Hamburg, Germany

⁶Department of Physics, University of Helsinki, Helsinki, Finland

* now at: International Institute for Applied Systems Analysis, Laxenburg, Austria

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Correspondence to: R. H. H. Janssen (ruud.janssen@wur.nl)

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We study the combined effects of land surface conditions, atmospheric boundary layer dynamics and chemistry on the diurnal evolution of biogenic secondary organic aerosol in the atmospheric boundary layer, using a model that contains the essentials of all these components. First, we evaluate the model for a case study in Hyytiälä, Finland, and find that it is able to well reproduce the observed dynamics and gas-phase chemistry. We show that the exchange of organic aerosol between the free troposphere and the boundary layer (entrainment) must be taken into account in order to explain the observed diurnal cycle in organic aerosol (OA) concentration. An examination of the budgets of organic aerosol and terpene concentration shows that the former is dominated by entrainment, while the latter is mainly driven by emission and chemical transformation. We systematically examine the role of the land surface, which governs both the surface energy balance partitioning and terpene-emissions, and the large-scale atmospheric process of vertical subsidence. Entrainment is especially important for the dilution of organic aerosol concentrations under conditions of dry soils and low terpene-emissions. Subsidence suppresses boundary layer growth while enhancing entrainment. Therefore it influences the relationship between organic aerosol and terpene-concentrations. Our findings indicate that the diurnal evolution of SOA in the boundary layer is the result of coupled effects of the land surface, dynamics of the atmospheric boundary layer, chemistry, and free troposphere conditions. This has potentially some consequences for the design of both field campaigns and large-scale modeling studies.

1 Introduction

A large part of sub-micron atmospheric particulate material is organic (Hallquist et al., 2009; Jimenez et al., 2009). Secondary organic aerosols (SOA) which are formed in the atmosphere from oxidation of high-volatility precursors are an important contributor

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to the total organic aerosol budget. The importance of this SOA in new particle formation (Metzger et al., 2010; Laaksonen et al., 2008; O'Dowd et al., 2002) and the growth of atmospheric particles to cloud condensation nuclei (Riipinen et al., 2011; Slowik et al., 2010; Tunved et al., 2006) is well established. Formation of SOA from gas-phase species depends on the emissions of these species and their processing in the atmosphere. When emitted at the land surface, they enter into the atmospheric boundary layer (BL), the lowest part of the atmosphere, which is characterized by strong turbulent motions that are largely influenced by the underlying land surface and the free troposphere (FT) on top of it (de Bruin, 1983; van Heerwaarden et al., 2009). Acting as a buffer between the surface processes and the FT, the BL dynamics affect the processing of aerosol precursor species and the partitioning into the aerosol phase of their low-volatility reaction products.

Here we aim to systematically study the role of the diurnal variability of dynamics and chemical transformation on the evolution of organic aerosol. We do this by modeling a case study and conducting a set of sensitivity analyses using MXLCH-SOA, a coupled model of BL-dynamics, land surface, gas-phase chemistry and gas/particle-partitioning, aiming to determine the role of different processes in controlling the diurnal variability in OA. A schematic overview of the studied system is given in Fig. 1. It is important to note that we strive for a balance between all relevant components of the system and therefore include the land surface, BL dynamics, chemistry and gas/particle-partitioning in a way that keeps the essentials of all components. This allows us to systematically study the whole system in a coupled approach while avoiding excessive complexity. Thus, we expand upon on modeling studies that take the diurnal variability of BL-characteristics on SOA-formation into account using box models with prescribed diurnal cycles of temperature, humidity, boundary layer height, and oxidants (Sheehan and Bowman, 2001; Bowman and Karamalegos, 2002; Dzepina et al., 2009) or applying a fixed BL-height, thereby neglecting the effects of entrainment on BL growth and reactant concentrations (Tunved et al., 2006; Riipinen et al., 2011). Besides, regional and global chemical transport models used for simulating SOA-formation are usually

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forced by offline meteorology (Lane et al., 2008; Slowik et al., 2010; Riipinen et al., 2011), which hinders the ability to study their sensitivity to meteorological and land surface boundary conditions. In contrast, in our approach the dynamics and chemistry are solved simultaneously, which allows for an analysis of different cases in which BL-growth and entrainment is driven by varying land surface and FT conditions. Moreover, in our approach we are able to explicitly calculate the contributions of the different processes to the budgets of reactants, since MXLCH-SOA contains basic parametrizations of the relevant processes based on sound physical and chemical assumptions.

As a first step we validate MXLCH-SOA with observations of BL-dynamics and gas-phase chemistry collected at the SMEAR II measurement station at Hyytiälä, Finland. It is located in the boreal forest which is an important source of SOA, mainly from terpene-oxidation (e.g., Tunved et al., 2006). Then we perform a budget analysis of the main contributions to terpene and organic aerosol mass in time, including emissions, entrainment, chemistry and partitioning. Finally we analyze the sensitivity of BL organic aerosol evolution to (1) the land surface conditions, in terms of surface heat flux partitioning, which drives the exchange between the FT and the BL, and terpene-emission and (2) land surface conditions (heat flux partitioning), entrainment and the large-scale atmospheric process of vertical subsidence associated with the presence of a high pressure system. The experiments are based on a case study for the boreal forest region. However, since our focus is on understanding the processes that occur in each BL in which SOA-formation occurs, we will discuss the general applicability of the findings for this case study and their implications for field-campaigns and large scale modeling.

2 Methods

In this section we briefly introduce the methods to represent the BL dynamics and gas-phase chemistry including SOA-formation through oxidation of volatile organic

compounds (VOCs) in MXLCH-SOA. Furthermore, we describe the case study and the numerical experiments that we performed.

2.1 Dynamics of the boundary layer: mixed layer approach

Mixed-layer theory (Lilly, 1968; Tennekes, 1973) is an approximation for mixing in the BL under convective conditions. Under this approximation scalars and chemical species are instantaneously and perfectly mixed throughout the BL due to the high turbulent intensity (Vilà-Guerau de Arellano et al., 2011). In this way, the mixed-layer approach is comparable to a homogeneous reactive box in which chemical transformations take place. Within this approach, the BL grows due to the entrainment of dry air at the interface between the FT and the BL, which is induced by the buoyancy flux at the surface. These processes influence the concentrations of reactive species due to the fact that the BL becomes higher, which increases the mixing volume, and because the air that is entrained from the FT typically contains different concentrations of reactive species. The importance of FT-BL exchange for the diurnal variability of reactants in the Amazon was already suggested by Martin et al. (1988) and Ganzeveld et al. (2008).

With respect to the surface conditions, the vegetated land surface forms the source of biogenic VOCs that are oxidized in the BL to form SOA. NO-emissions from the soil influence atmospheric NO_x -levels and consequently the formation of the oxidants ozone (O_3) and the hydroxyl radical (OH). In this study, we prescribe surface fluxes of sensible (H) and latent heat (LE), VOCs and NO. The FT conditions for temperature, moisture and reactants are also imposed, both in terms of their initial value and, in case of temperature and moisture, their lapse rate. Reactive species in the FT are affected by chemical transformations, but have an assumed constant concentration profile. Initial and boundary conditions are obtained from fitting the MXLCH-SOA to the case study observations.

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2.2 Gas-phase chemistry

The chemical mechanism used to represent the essentials of the O₃-NO_x-VOC-HO_x-chemistry is given by Reactions (R1)–(R19) in Table 1. It is based on and further extends the simplified reaction schemes used by Krol et al. (2000) and Vilà-Guerau de Arellano et al. (2011). It is able to capture the essential photochemistry of the main reactive species in rural and remote areas with low anthropogenic influence. O₃-deposition follows a sinusoidal profile during the day (Table 5). In this way, the deposition velocity of O₃ scales with stomatal resistance and LE (e.g. Ganzeveld et al., 2008).

A simple reaction mechanism to simulate SOA formation is introduced in MXLCH. In this mechanism, semi-volatile compounds that are able to partition into the aerosol phase are generated by the first-step oxidation of terpenes by O₃ and OH. Further chemical ageing is not represented. The SOA-forming reactions are shown in Table 1 (Reactions R20 and R21) and the stoichiometric coefficients in Table 2. For all simulations we assumed low NO_x-conditions, i.e. that organic peroxy radicals react predominantly with HO₂ or RO₂ and not NO, which is a reasonable approximation for the conditions of our study.

All terpenes in our model are assumed to behave as α -pinene. The total terpene-concentration is the sum of the measured concentrations of 8 terpenes by Spirig et al. (2004). In the experiments, we used TERP, a generic terpene with the properties of α -pinene, but with emissions scaled up to reproduce the total terpene concentration. Hao et al. (2011) show that for low VOC-concentration ($< 5 \mu\text{g m}^{-3}$) the assumption that SOA-yields for α -pinene and real plant emissions are similar is justified. Furthermore, we assumed that aerosol yields from α -pinene with OH are equal to the better documented yields for ozonolysis of α -pinene. The information on OH-initiated oxidation in the literature is limited. Hao et al. (2011) reported a higher volatility and thus lower yields from OH-dominated chemistry than for O₃-initiated oxidation. In contrast, there are other experiments which show that OH yields are a little higher than the O₃

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yields (N. Donahue, personal communication, 2011; Henry and Donahue, 2011). Finally, we assumed that aerosol formation from isoprene can be neglected due to the low concentrations of this precursor at our study location (e.g., Spirig et al., 2004).

Terpene emissions are prescribed with a sinusoidal profile during the day with a maximum as specified in Table 3. The sinusoidal form of the diurnal emission is supported by the terpene-flux measurements of Rinne et al. (2007). The prescribed terpene fluxes lie within the range of the measurements by Rinne et al. (2007) for similar temperatures and at the same location, but are higher than the estimates for the same dataset with the mixed layer gradient method by Spirig et al. (2004). One reason for this discrepancy could be the fact that the method used by Spirig et al. (2004) did not account for entrainment and therefore underestimates dilution of the terpenes in the BL.

2.3 Organic aerosol formation: gas/particle-partitioning

Gas/particle-partitioning is dominated by absorption of semi-volatile species into an organic aerosol phase (Pankow, 1994). We assume that the semi-volatile terpene oxidation products are in thermodynamic equilibrium with the aerosol phase, which means that partitioning occurs instantaneously. We account for gas/particle-partitioning in MXLCH-SOA by implementing the volatility basis set approach (Donahue et al., 2006). This approach lumps the numerous semi-volatile products that are formed after VOC-oxidation into several bins with logarithmically spaced effective saturation concentrations. The mass yields for the different bins are obtained by fitting results from laboratory studies of SOA-formation. Here, we use 4 bins with effective saturation concentrations of 1, 10, 100 and 1000 $\mu\text{g m}^{-3}$ at 298K, respectively, encompassing a relevant range of product vapor pressures (Lane et al., 2008). The mass stoichiometric coefficients for the different bins are taken from Tsimpidi et al. (2010), see Table 2. At each time step, the total organic aerosol concentration C_{OA} is diagnosed from:

$$X_{p,i} = \left(1 + \frac{C_i^*}{C_{\text{OA}}}\right)^{-1} ; \quad C_{\text{OA}} = \sum_i (X_{p,i} C_i) + \text{OA}_{\text{BG}} \quad (1)$$

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where $X_{p,i}$ is the fraction of compound i in the aerosol phase ($-$), C_i^* the effective saturation concentration of compound i ($\mu\text{g m}^{-3}$), C_{OA} is the total organic aerosol mass concentration ($\mu\text{g m}^{-3}$) and OA_{BG} is the background organic aerosol concentration ($\mu\text{g m}^{-3}$).

Temperature dependence of the saturation concentrations follows Clausius-Clapeyron (Sheehan and Bowman, 2001):

$$C_i^* = C_{i,0}^* \frac{T_0}{T} \exp \left[\frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_0} - \frac{1}{T} \right) \right] \quad (2)$$

in which $C_{i,0}^*$ is the effective saturation concentration of compound i at reference temperature T_0 (here 298K), T is the actual temperature (K), ΔH_{vap} is the enthalpy of vaporization (kJ mol^{-1}) and R is the ideal gas constant ($\text{J mol}^{-1} \text{K}^{-1}$). Here, we follow Pathak et al. (2007) and set ΔH_{vap} to 30 kJ mol^{-1} for all condensable products.

A background C_{OA} of $0.8 \mu\text{g m}^{-3}$ and of $0.2 \mu\text{g m}^{-3}$ is assumed for the BL and FT, respectively. The BL-value is based on the measurements by Raatikainen et al. (2010). These measurements are made in the canopy and therefore serve as an estimate of the order-of-magnitude for the BL concentration. Since a FT value is not available from measurements, we have performed an analysis to determine the sensitivity to the assumed value, presented in Sect. 3.2. The background organic aerosol in BL and FT is assumed to be aged and thus non-volatile and will therefore not repartition back into the gas phase (Cappa and Jimenez, 2010).

Figure 2 shows the sensitivity of the calculated partitioning coefficient for the first bin ($X_{p,1}$) and C_{OA} to variations in T and OA_{BG} for a range of typical values for this study. While the response of $X_{p,1}$ to variations T and OA_{BG} is quite non-linear, especially at for low T and high OA_{BG} , the response of C_{OA} is nearly linear to changes in OA_{BG} . This is due to the fact that the strongest non-linear behavior of $X_{p,1}$ is found for conditions where OA_{BG} makes up the largest part of C_{OA} and therefore the partitioning of semi-volatile species C_1 into the aerosol phase plays only a minor role in determining

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C_{OA} . The sensitivities of the partitioning coefficients of the other bins show similar patterns.

2.4 Observational evaluation: case study

To evaluate our modeling approach we selected a dataset of surface and boundary layer characteristics (both dynamics and chemistry) that is as complete as possible. Our assumption of a well-mixed boundary layer is justified for sunny days characterized by convective turbulent conditions. To meet these two requirements, we selected observations from 8 August 2001 at the SMEAR II field station at Hyytiälä (61°51' N, 24°17' E) in Southern Finland, where ecosystem, meteorological, trace gas and aerosol properties are measured since 1996 (Hari and Kulmala, 2005).

The observed surface fluxes of sensible (H) and latent heat (LE) are used as forcings for our model and are therefore prescribed as boundary conditions. The model simulation covers 11 h, beginning at 07:50 LT (sunrise is at 07:30 LT). The diurnal evolution of temperature, humidity, O_3 and NO_x , observed at 67.2 m – the highest measurement level available at 52 m above the canopy – and obtained using the SMEAR Smart-Search database (Junninen et al., 2009), is used to determine the ability of the model to reproduce the diurnal variability in the BL. In addition, observations of BL-height from temperature and humidity profiles and BL-concentrations of terpenes gathered with a tethered balloon (Spirig et al., 2004) enable us to complete the validation.

2.5 Numerical strategy

We designed a series of numerical experiments to investigate the dependence of the SOA evolution on the chemical and dynamical processes and their relationships as depicted in Fig. 1. In the first experiment, we study the sensitivity of C_{OA} to the surface conditions. The sensitivity analysis is carried out as a function of the evaporative fraction (EF) and the terpene emission flux (F_{TERP}) (indicated by (1) in Fig. 1). EF is defined as $LE/(H + LE)$ – i.e., it is the fraction of the surface heat flux that is used

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for evaporation of water from the surface. In the second experiment, we evaluated the sensitivity of C_{OA} to EF and to large-scale vertical subsidence motions (indicated by (2) in Fig. 1). The latter are due to the presence of synoptic high pressure systems that suppress the BL-growth. In these analyses, we studied C_{OA} at the end of the day (18:50), because then BL-growth and entrainment cease and we can evaluate the net effect of the day-time dynamics, emissions and chemistry.

3 Results

3.1 Model evaluation

Figure 3 shows the time evolution of the dynamic variables for the initial and boundary conditions as specified in Table 4: the surface heat fluxes (H and LE), boundary layer height (h), mixed layer potential temperature ($\langle\theta\rangle$) and specific moisture ($\langle q\rangle$). The onset of the prescribed surface heat fluxes is delayed by about one hour, as compared to the measurements. By so doing, we ensure that the model calculations begin within the well-mixed assumptions, when the ground thermal inversion is already broken. Both H and LE fall within the low end of the observations. This results from fitting the model to observed θ , q and h and could be due to the different footprints of the heat fluxes and θ and q : H and LE are measured at 23 m, while θ and q are observed at 67.2 m and consequently the measurements of H and LE represent a smaller area.

The time evolution of $\langle\theta\rangle$ and $\langle q\rangle$ is reproduced well. This satisfactory agreement of the $\langle\theta\rangle$ and $\langle q\rangle$ -evolution demonstrates that the model is capable to reproduce the entrainment process well for a given set of surface heat fluxes. Although only one observation is available at 12:20, the calculated BL-height is similar to the measured height of 1000 m.

The diurnal trends in the chemical species (Fig. 4), with initial concentrations and surface fluxes as specified in Table 5 agree well with the observations. This confirms that the processes of entrainment, emission and chemistry (see Fig. 1) and their influence

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on the time evolution of the chemical species are simulated well. The evolution of O_3 is the result of entrainment of O_3 from the FT, especially during the rapid growth of the BL during the morning, a net positive chemical production during the day and its removal by dry deposition. Averaged over the day, the entrainment flux is about 1.4 times as large as the deposition flux, but in the early morning (08:00) the entrainment flux is 8 times larger than the deposition flux. This is due to the fact that the O_3 -deposition flux follows a sinusoidal form during the day (Table 5), which has a minimum in the morning. The NO_x measurements must be interpreted carefully since the NO_2 ones are probably affected by error in the measurement procedure (P. Keronen, Univ. of Helsinki, personal communication, 2011). NO_2 measurements are scaled down to match an observed NO_2/NO ratio of 5 as obtained from more reliable measurements in summer 2010 at the same location (P. Keronen, personal communication, 2011). In spite of the large uncertainty regarding the NO_x measurements, we are able to satisfactorily reproduce the order of magnitude of the observed NO_x -concentrations. Calculated OH-concentrations range from 4×10^5 at the end of the day to 4.5×10^6 molec cm^{-3} in the late morning. Unfortunately, no observations of OH in the mixed layer (above the canopy) are available for this environment. Petäjä et al. (2009) report an observed diurnal range in in-canopy OH-concentrations in the order of 10^4 to 10^5 molec cm^{-3} . BL-concentrations are likely higher, because of the higher O_3 -concentration and light-intensity and lower concentrations of VOCs, which deplete OH. We find, however, that C_{OA} is not very sensitive to OH-levels. For the case study, increasing the OH-concentration by a factor 2 resulted in an increase of C_{OA} at the end of the day of only 1% and reducing it by a factor 2 in a decrease of 3%. The reason for this weak sensitivity will be further discussed in Sect. 3.3.

Figure 5 shows the results for terpenes with emission fluxes as specified in Table 3. MXLCH-SOA is able to reproduce the order of magnitude of the observed concentrations of both α -pinene and the sum of terpenes ($\langle TERP \rangle$). Since there are only four data points and the error in the individual measurements is large, we cannot draw conclusions on how well we can reproduce the diurnal evolution of the terpene-concentrations

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from these data. Typically, terpene concentrations will increase during nighttime (e.g., Ruuskanen et al., 2009) due to temperature-driven emissions into a BL that is shallow and stably stratified. Besides, it is characterized by low O_3 -concentrations and consequently low chemical destruction. A sensitivity analysis revealed that the diurnal cycle in C_{OA} is not very sensitive to the initial terpene-concentration. The reason for this will be discussed further in Sect. 3.3.

Overall, comparison of the model results with the observations shows that we can reproduce the time evolution of the dynamics and the order-of-magnitude of the gas-phase chemistry well, which gives confidence in the validity of MXLCH-SOA for further analyses.

3.2 Diurnal evolution of organic aerosol

A key aspect of this study is the ability of MXLCH-SOA to model the organic aerosol concentration C_{OA} as a function of dynamics and chemistry (Fig. 1). As expressed in Eq. (1), the background organic aerosol concentration OA_{BG} affects C_{OA} both directly and indirectly by influencing the partitioning into the aerosol phase of the semi-volatile reaction products (C_i) that result from TERP-oxidation. Therefore, to understand the diurnal evolution of C_{OA} it is crucial to represent the OA_{BG} accurately, both in the BL and the FT, the latter since OA_{BG} from the FT is entrained into the BL during its growth.

Unfortunately, there are no observed vertical C_{OA} profiles for this environment, which could help constrain our numerical experiments (Heald et al., 2011). In order to determine the sensitivity of the diurnal cycle in C_{OA} to the FT OA_{BG} , we carry out 4 identical numerical experiments, only varying the OA_{BG} in the FT (Fig. 6). By so doing, we are able to study the influence of the OA_{BG} in the residual layer (the remainder of the BL from the previous day) that was decoupled from the nocturnal boundary layer. We included a case for which BL and FT concentrations are equal. This may not be realistic, because we simulate biogenic OA only, which has a surface source and thus lower concentrations in the FT; however, the high FT biogenic OA is shown for illustrational purposes. Since we expect that C_{OA} is much lower in the FT than in the BL, the other

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three cases represent FT OA_{BG} of 0.0, 0.2 and $0.4 \mu\text{g m}^{-3}$, respectively. For all these cases, we find a net decrease of C_{OA} during the day. Without further observational constraints on the actual FT-concentration, we assumed a value of $0.2 \mu\text{g m}^{-3}$ for the numerical experiments presented hereafter.

There are only few measurements of organic aerosol concentrations for the location of our case study and as a result we are not able to directly compare modeled with measured data. There are, however, observations available at the same site that allow us to qualitatively compare the diurnal behavior of OA. Raatikainen et al. (2010) measured organic aerosol concentrations at Hyytiälä during 15 days in spring 2005. They identified two oxygenated organic aerosol (OOA) groups. One of them (OOA2) has a clear diurnal cycle, has undergone little oxidation and is qualified as originating from local sources, the most likely being the oxidation of locally emitted VOCs based on the observation that the presence of OOA2 is independent of air mass history. Therefore, it is interesting to compare the diurnal cycle of OOA2 with the simulated C_{OA} and we include the OOA2-data in Fig. 6. The measured OOA2 shows a similar concentration decrease during the day as the modeled C_{OA} . This further indicates the need to have a balanced approach in calculating the C_{OA} taking into account emission, dynamical processes like entrainment and chemical transformations (Fig. 1). The absolute concentrations should be compared with care, however, since the measurements were performed inside the canopy while the model results reflect BL averages.

3.3 Budgets

To deepen our understanding of the concentration tendencies, we make use of the ability of the mixed-layer model to calculate the different contributions of entrainment, emissions and chemistry to the total tendency of chemical species (Tennekes, 1973; Vilà-Guerau de Arellano et al., 2011), in this case C_{OA} and TERP. The TERP-budget

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reads:

$$\frac{d\langle\text{TERP}\rangle}{dt} = \overbrace{\frac{F_{\text{TERP}}}{h} \sin\left(\frac{\pi t}{t_d}\right)}^{\text{emission}} + \overbrace{\frac{w_e \Delta\text{TERP}}{h}}^{\text{entrainment}} - \overbrace{\sum_j (k_j \langle\text{TERP}\rangle \langle\text{OX}_j\rangle)}^{\text{chemistry}} \quad (3)$$

F_{TERP} is the maximum daily terpene emission flux ($\mu\text{g m}^{-2} \text{h}^{-1}$), as specified in Table 3, h is the BL height (m), t is the time since the start of the simulation (s), t_d the length of the simulation (s), w_e is the entrainment velocity (m s^{-1}), which in absence of subsidence equals BL-growth (dh/dt), ΔTERP is the TERP-concentration jump between the BL and the FT ($\mu\text{g m}^{-3}$) (with the jump of a scalar or reactant C defined as $\Delta C = C_{\text{FT}} - \langle C \rangle$, see also Fig. 10), k_j is the reaction rate of TERP with oxidant OX_j (either O_3 or OH) and $\langle\text{OX}_j\rangle$ the mixed layer concentration of oxidant OX_j . Note that h , w_e , ΔTERP , $\langle\text{TERP}\rangle$ and $\langle\text{OX}\rangle$ are calculated simultaneously during the MXLCH-SOA runs and therefore account for the coupling between dynamics and chemistry. This defines the difference between our approach and using box models with a fixed h or a BL-growth calculated from measurements: here, the development of the BL and entrainment are governed by the diurnal dynamics of temperature and moisture, through w_e in the second term on the right hand side (RHS) of Eq. (3), which result from the coupling of the BL with the land surface and the FT.

Figure 7 shows the budget of TERP and the relative contribution to the total chemical tendency of the reaction of TERP with O_3 and OH , respectively, for the case study. Overall, emission and chemistry contribute about equally to the budget (Fig. 7a). The prescribed F_{TERP} is low in the early morning, but since the BL is still shallow, the emission term contributes strongly to the TERP-budget during the course of the morning and becomes the most important term with a maximum of $0.4 \mu\text{g m}^{-3} \text{h}^{-1}$ at 10:00. After this time, the BL height increases rapidly, which decreases the importance of this term. The chemistry (Fig. 7b) is dominated by the destruction by OH , so the late morning peak in the chemistry term is associated with the peak in OH that occurs then. The

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contribution of O_3 to the chemical destruction of TERP is 25 % during the day, but becomes dominant in the evening as OH is reduced. Entrainment contributes significantly to the total tendency between 9 and 12 when BL growth is strongest with 230 m h^{-1} . The maximum contribution of entrainment to the total tendency of TERP is about 20 % of the contribution of the emission. During most of the morning, the TERP-tendency is positive, mainly due to the emissions, but at the end of the afternoon, the tendency becomes negative due to the fact that chemical destruction continues while the emissions decrease.

Damköhler numbers (the ratio of the turbulent time scale to the chemistry time scale) for TERP range from 0.05 to 0.2. Under this regime of relatively slow chemistry, the emission and entrainment (term 1 and 2 on the RHS of Eq. 3) play an important role. This further confirms the importance of the atmospheric transport and turbulence for the behavior of TERP.

Similar to Eq. (3) for TERP, we can explicitly calculate the budget of C_{OA} :

$$\frac{dC_{\text{OA}}}{dt} = \frac{\overbrace{w_e \Delta \text{OA}_{\text{BG}}}^{\text{OA}_{\text{BG}}\text{-entrainment}}}{h} + \sum_i X_{p,i} \left[\frac{\overbrace{w_e \Delta C_i}^{C_i\text{-entrainment}}}{h} + \overbrace{\sum_j \alpha_i k_j [\text{TERP}][\text{OX}_j]}^{C_i\text{-chemistry}} \right] \quad (4)$$

Here, $\Delta \text{OA}_{\text{BG}}$ is the jump in the background organic aerosol concentration between the BL and the FT ($\mu\text{g m}^{-3}$) and α_i is the stoichiometric coefficient for the oxidized semivolatile product C_i (see Table 2). Note that for the C_{OA} budget, contrary to the TERP budget, there is no emission term since the aerosol is either of secondary origin or present as a background concentration. This is justified since our budget is focused on the submicron OA concentrations, while primary biological particles (PBAP) are thought to be important only for the supermicron mode (Pöschl et al., 2010).

The evolution of C_{OA} is thus the result of a combination of the influence of the OA_{BG} originating from the FT and the newly formed condensable species from the oxidation of TERP (Fig. 5b). Entrainment of background OA dominates the budget of C_{OA}

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(Fig. 8): during the morning, the OA that was concentrated in the shallow BL during the night is diluted when the BL grows and air from the FT with a lower OA_{BG} -concentration is entrained. The importance in our simulations of the background OA level in the FT stresses the importance to have upper air measurements (Heald et al., 2011) to understand the evolution of C_{OA} in the BL. The semi-volatile products C_i have net production throughout the day, but their contribution to the C_{OA} budget is relatively small. Only at the end of the day (from 15:30 onwards), there is a net positive tendency of C_{OA} , since the BL-growth becomes negligible and the partitioning of terpene C_i to the particle phase outweighs the entrainment term.

These tendencies show that for TERP and C_{OA} , emissions, chemistry and entrainment play a different role, which is important to understand the results of the sensitivity analyses, presented in Sect. 3.4. Since TERP is a reactive species with a relatively short lifetime and no background concentration, the relative importance of chemistry in its budget is larger than for OA, which does have a long lived background with a typical lifetime of a week.

To quantify the importance of the newly formed SOA from TERP oxidation (OA_{TERP}) versus the OA_{BG} that is initially present and mixed in from the FT, we define a fresh SOA to background OA ratio:

$$r_{FB} = \frac{OA_{TERP}}{OA_{BG}} \quad (5)$$

This ratio can be interpreted as follows: for $r_{FB} \ll 1$ the OA_{BG} dominates and the C_{OA} will be determined by the dilution of this background organic aerosol. When $r_{FB} \sim 1$, there is an equal contribution of background and newly formed OA. For $r_{FB} \gg 1$, the C_{OA} is determined completely by the formation of SOA during the day. However, values of $r_{FB} \gg 1$ are not expected to be common, since the partitioning of the semi-volatile products into the aerosol phase depends on OA_{BG} (see Eq. 1). For an initial OA_{BG} in the FT of $0.2 \mu\text{g m}^{-3}$, the $r_{FB} = 0.22$ at 18:50. This further demonstrates the dominating effect of the background aerosol on the C_{OA} in the BL for the case study.

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3.4 Sensitivity analysis

3.4.1 Response of C_{OA} to land surface conditions

As shown in the previous budget analyses, it is important to reproduce accurately both the BL dynamics and chemistry tendency since they together determine the concentration of a given species. We therefore extend our analysis to analyze the role of land surface in driving both dynamics and chemistry. The land surface determines how much terpenes are emitted and into which mixing volume by regulating the partitioning between sensible and latent heat flux (see Fig. 7 of the TERP-budget). The partitioning of the heat flux governs the growth of the BL, with a much larger growth when sensible flux dominates over latent heat flux ($EF \sim 0$), i.e. for dry surface conditions. Under these conditions, the sensible heat flux will strongly heat the BL, which decreases the temperature jump between the BL and FT. This further facilitates the entrainment of warm air from the FT into the BL which subsequently enhances the BL growth. Conversely, the BL grows less rapidly when latent flux dominates ($EF \sim 1$) under very moist surface conditions. This is due to the fact that for a high EF, most available energy is used to evaporate water from the surface and there is little left for BL-growth. In Fig. 10, typical vertical profiles of θ and q are sketched, to illustrate these effects. Therefore, our first sensitivity analysis addresses the role of different combinations of evaporative fraction (EF) and terpene emission flux (F_{TERP}) on the diurnal evolution of C_{OA} . We explore the complete range of possible conditions of EF: from a BL driven solely by the sensible heat flux ($EF = 0$) to a BL driven only by the evaporation flux ($EF = 1$). Similarly, F_{TERP} ranges from 0 to $1 \text{ mgm}^{-2} \text{ h}^{-1}$, which encompasses the range of terpene-fluxes observed at the SMEAR II station (Rinne et al., 2007).

Figure 9a shows the calculated C_{OA} and TERP-concentration at 18:50. The conditions of EF and F_{TERP} for the case study discussed above are indicated in the figure. As expected, C_{OA} always increases with larger F_{TERP} due to the higher formation rate of biogenic SOA. It also increases with EF because shallower boundary layers, weaker entrainment and thus less mixing of FT air with low OA-concentrations occur when the

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land surface is dominated by the evaporation flux. The effect on temperature acts in the same direction, i.e. a higher EF leads both to a lower sensible heat flux into the BL and to less entrainment of relatively warm free tropospheric air. Consequently, the temperature in the mixed layer becomes lower. The temperature decreases by 6 K in the experiment going from $EF = 0$ to $EF = 1$. Because of the lower temperatures, more semi-volatile material will partition into the aerosol phase, but this has only a minor effect compared to the changes in dilution. This becomes clear from the partitioning coefficient X_p , which is shown together with C_{OA} in Fig. 9a for semi-volatile product C_1 . X_p depends on C_{OA} and T , following Eqs. 1 and 2. Here, we find that X_p closely follows the behavior of C_{OA} and only a slight deviation from this pattern is caused by the dependence of X_p on T . The T -dependence is the most pronounced for low EF, when a large sensible heat flux leads to a larger heating of the BL and consequently a large entrainment of relatively warm air from the FT.

Based on the relationship between C_{OA} and TERP concentration, we can distinguish 2 different regimes: one characterized by soils with low moisture content ($EF < 0.5$) and low terpene emissions ($F_{TERP} < 0.6$) and another characterized by high moisture content (i.e., wet soil) and strong terpene emissions. Dry soil causes larger sensible heat fluxes, which lead to rapid BL-growth and enhance dilution of C_{OA} due to entrainment of air from the FT. For TERP, on the other hand, the entrainment term has a minor contribution to the total tendency (due to the lower lifetime of this species), which is dominated by the emissions and the chemical destruction (see Fig. 7). Since C_{OA} and TERP are dominated by different processes in this regime, their tendencies are not strongly related. In this regime, the role of entrainment will dominate over that of chemistry. For a wet soil ($EF > 0.5$) and high emissions ($F_{TERP} > 0.6$), on the other hand, we are in a regime where chemistry plays a larger role in determining the tendency of C_{OA} . Here, the larger emission contributes more to the C_{OA} -tendency, while the low sensible heat flux results in weak BL-growth and entrainment. The combined effect of higher emissions into shallower BL causes a significant contribution of chemistry to the C_{OA} -tendency. Only in the upper right corner of Fig. 9, we find conditions for which

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there is a net increase of C_{OA} during the day, since here condensation outweighs entrainment. These conditions are delimited by the black contour. In this regime, C_{OA} and TERP are strongly related since there the influence of entrainment is relatively small. The consequences of this sensitivity of C_{OA} for conditions of the case study can be deduced from Fig. 9a. C_{OA} at a terpene emission flux of $304 \text{ mgm}^{-2} \text{ h}^{-1}$ ranges from 0.30 to $0.62 \mu\text{gm}^{-3}$, a difference of a factor 2, when the EF increases from 0 to 1. For a constant EF of 0.25 and F_{TERP} ranging from 0 to $1 \text{ mgm}^{-2} \text{ h}^{-1}$, C_{OA} could range from 0.26 to $0.49 \mu\text{gm}^{-3}$, a difference of almost a factor 2. On the other hand, in the dry regime with a low emission there is a large range of conditions of EF and F_{TERP} which can lead to a certain observed C_{OA} . An observed C_{OA} of $0.31 \mu\text{gm}^{-3}$, as in the case study, could result from EF = 0 and $F_{\text{TERP}} = 0.4$, but also from EF = 0.9 and $F_{\text{TERP}} = 0$.

Figure 9b shows the behavior of r_{FB} as a function of EF and F_{TERP} . The entrainment and chemistry limited regimes are also well developed: for low EF and F_{TERP} the background aerosol dominates, while for wet soils (EF > 0.3) and $F_{\text{TERP}} > 0.4$, r_{FB} becomes larger than 1, meaning that there is more OA_{TERP} present than OA_{BG} . There is a wide range of conditions for which they are equally important: from EF = 1 and $F_{\text{TERP}} \sim 0.4$ to EF ~ 0.3 and $F_{\text{TERP}} = 1$.

3.4.2 Combined response of C_{OA} to subsidence and land surface conditions

As indicated in Fig. 1 and in order to complete our analysis, it is interesting to analyze the role of subsidence because on summer days, high pressure systems typically prevent the BL-growth by inducing downward air motions. This was, for example, the case over Finland during the HUMPPA-COPEC-campaign in summer 2010 (Williams et al., 2011). Further, the soil moisture content determines the partitioning of the surface heat fluxes and thus the energy that is available for BL-growth and entrainment.

To understand the influence of subsidence, it is important to note that its effect is twofold: it suppresses BL-growth while simultaneously enhancing entrainment. The suppression of BL-growth becomes clear when looking at the equation for BL-growth,

which is the net result of the entrainment velocity w_e on one hand and the subsidence velocity w_s on the other:

$$\frac{dh}{dt} = w_e + w_s \quad (6)$$

In the analysis, we prescribe the large-scale subsidence rate (ω (s^{-1})), defined as the divergence of the horizontal mean wind. It can be thought of as the fraction with which the BL is pushed down each second. The subsidence velocity (w_s (ms^{-1})), with a typical order of magnitude of $10^{-2} ms^{-1}$, is therefore in our modeling approach represented as:

$$w_s = -\omega h \quad (7)$$

To understand the effects of subsidence on entrainment, we need to analyze the expression to calculate w_e . It is a function of the buoyancy flux and the virtual potential temperature jump between the BL and the FT ($\Delta\theta_v$) (van Heerwaarden et al., 2009):

$$w_e = \frac{\overline{\beta(w'\theta'_v)_s}}{\Delta\theta_v} \quad (8)$$

where β is the (fixed) ratio between the surface and entrainment buoyancy flux (dimensionless), $\overline{(w'\theta'_v)_s}$ the surface buoyancy flux (Kms^{-1}) and $\Delta\theta_v$ is the jump of the virtual potential temperature between the BL and FT, defined as:

$$\Delta\theta_v = \Delta\theta + 0.61(\langle q \rangle \Delta\theta + \langle \theta \rangle \Delta q + \Delta\theta \Delta q) \quad (9)$$

$$\simeq \Delta\theta + 0.61\langle \theta \rangle \Delta q \quad (10)$$

where $\Delta\theta$ and Δq are the differences in θ and q between the BL and the FT, respectively. Figure 10 shows sketches of typical vertical profiles of θ , q , θ_v and C_{OA} for conditions with and without subsidence to illustrate these effects.

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For a constant EF, the buoyancy flux and therefore the numerator in Eq. (8) remains constant. Consequently, subsidence only affects w_e through $\Delta\theta_v$. In case of subsidence, the same amount of sensible heat is introduced into a shallower BL, so $\langle\theta\rangle$ increases and $\Delta\theta$ decreases. The specific moisture ($\langle q \rangle$), however, decreases with subsidence, because the increase in moisture due to evaporation into a smaller mixing volume is offset by the enhanced entrainment of dry air. Δq is therefore smaller in the case with subsidence. Taken together, these effects result in a smaller $\Delta\theta_v$ in case of subsidence: the effect of $\Delta\theta$ on $\Delta\theta_v$ is only partly compensated by the effect of Δq , through the second term on the RHS of Eq. (10). In all our experiments, we find that w_e is enhanced when subsidence increases. This means that the enhanced entrainment due to a stronger heating of the BL is further enhancing itself by diminishing $\Delta\theta_v$. For EF = 1, the daily average w_e ranges from 1 cm s^{-1} when there is no subsidence to 2 cm s^{-1} for $\omega = 1 \times 10^{-4} \text{ s}^{-1}$.

Figure 11a shows the sensitivity of C_{OA} to EF, ranging from 0 to 1, and subsidence ranging from no subsidence ($\omega = 0 \text{ s}^{-1}$), to strong subsidence ($\omega = 1 \times 10^{-4} \text{ s}^{-1}$). By increasing EF, BL-height decreases and both C_{OA} and TERP-concentration increase. As in the previous sensitivity analysis, the highest sensitivity is found for wet soils. BL-height decreases rapidly when $\text{EF} > 0.8$, which leads to an increase of C_{OA} by $\sim 50\%$ over the whole subsidence range, e.g. from 0.31 to $0.44 \mu\text{g m}^{-3}$ at $\omega = 5 \times 10^{-5} \text{ s}^{-1}$. TERP-concentration doubles for an EF ranging from 0.8 to 1.0, e.g. from 0.24 to $0.48 \mu\text{g m}^{-3}$ at $\omega = 5 \times 10^{-5} \text{ s}^{-1}$. However, C_{OA} decreases, while TERP-concentrations increase with stronger subsidence. For C_{OA} , this is because there is a stronger dilution due to entrainment with increasing subsidence. Since OA has a large background fraction compared to the production of SOA from TERP (Fig. 8), the enhanced dilution means that C_{OA} decreases despite the lower BL-height. TERP-concentrations, on the other hand, increase with larger subsidence values, because they are emitted into a shallower BL. Enhanced entrainment partly compensates for this, but has only a small effect on the TERP concentration due to the relatively short lifetime of this species (see also Fig. 7). The consequence is that under all conditions considered in

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our case study, the behavior of C_{OA} is unrelated to that of TERP, due to the different roles that entrainment, emission and chemistry have on their respective budgets.

Figure 11b shows the behavior of r_{FB} for varying subsidence and EF. r_{FB} is always below 1, because of the low formation of OA_{TERP} due to a low F_{TERP} . It increases with EF, because both C_{OA} , which enhances the partitioning into the aerosol phase, and TERP increase. For a changing ω and low EF (< 0.8), it decreases with increasing ω , because the enhanced dilution of OA_{BG} affects the partitioning negatively. For EF > 0.8 , however, r_{FB} shows some interesting non-linear behavior: at $\omega = 4 \times 10^{-5}$, r_{FB} has a maximum, because there the combination of a high TERP-concentration and a high X_{p} , caused by high C_{OA} , result in the partitioning of a large fraction of C_i into the aerosol phase.

4 Conclusions

We have studied the integrated effects of land surface, chemistry, and entrainment on the diurnal evolution of SOA, using MXLCH-SOA, a model that reproduces the dynamics of a diurnal convective atmospheric boundary layer and the chemical transformations of terpenes and their oxidants that lead to SOA-formation (Fig. 1).

MXLCH-SOA is able to reproduce the diurnal variability of SOA production and relate it with the observed dynamics and gas-phase chemistry for a characteristic case study in the boreal forest. Our findings indicate the importance of including entrainment to explain the observed diurnal cycle in SOA concentration, and suggest that entrainment may contribute ten times more to the total tendency than SOA production during day-time. This contribution is due to large volume of air that is entrained from the residual layer during the rapid growth of the boundary layer in the morning. A sensitivity analysis further suggests that the boreal forest is in a regime where relatively low terpene emissions are the limiting factor for SOA formation. For environments or situations with wet soils and high VOC emissions, e.g. the tropics, the effects of entrainment may be weaker and the SOA concentration and VOC concentration may therefore

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show a stronger relationship. Furthermore, we also find that under conditions of subsidence there is no straightforward relation between organic aerosol concentrations and terpene concentration.

Measured SOA and VOC concentrations are the net result of emissions, chemistry and dynamics. To interpret these measurements, it is important in the design of field campaigns to include observations of all of these components. More specifically, the role of the increase of SOA during the night both in the residual layer and in the nocturnal stable boundary layer will be an important factor to understand, since for most studied situations, the SOA evolution during day-time is mainly driven by entrainment. Therefore it is essential to have early-morning profiles of C_{OA} , to characterize both the initial concentration in the nocturnal stable BL and the organic aerosol that has built up in the residual layer, because this will be entrained into the convective boundary layer during the morning. Further, to understand ambient SOA concentrations, it may be equally important to characterize BL height and entrainment as it is to understand the temperature dependence of the saturation concentration of the semi-volatile species.

Our findings are also important for regional and global modeling studies: the strong sensitivity of C_{OA} to land surface and FT conditions means that uncertainties in the representation of these components may strongly affect the simulated C_{OA} . To model C_{OA} accurately, large-scale models should be able to reproduce the coupling between the land surface, boundary layer dynamics, free troposphere conditions and chemistry and the resulting behavior of organic aerosol and terpene concentration as presented in the sensitivity analyses. These analyses, presented in Figs. 9 and 11, can be used to quantify the uncertainty that arises from unaccurately representing these processes in large-scale models. Besides, our results indicate that box-models are only applicable for studying ambient SOA-formation when they account for boundary layer growth and entrainment and when background organic aerosol levels are well constrained.

Future research on the diurnal evolution of SOA concentrations will include an interactive land surface, since both surface heat fluxes (van Heerwaarden et al., 2009) and terpene emissions (Guenther et al., 1995; Niinemets et al., 2010) are the result of

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the interaction of the BL with the land surface. In summary, our findings indicate that in order to understand the diurnal evolution of SOA in the boundary layer the coupled effects of the land surface, dynamics of the atmospheric boundary layer, chemistry, and free troposphere conditions should be studied simultaneously. A balanced representation of all these processes should be considered when preparing and conducting both field campaigns and modeling.

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Table 1. Chemical reaction scheme used in the numerical experiments of MXLCH-SOA. In the reaction rate functions, T is the absolute temperature and χ is the solar zenith angle. First-order reaction rates are in (s^{-1}) and second-order reactions are in ($\text{cm}^3 \text{molec}^{-1} \text{s}^{-1}$). PRODUCTS are reaction products which are not further evaluated in the chemical reaction scheme. In Reaction (R17), $n = 0$ (no OH-recycling). $\alpha_1 - \alpha_4$ are stoichiometric coefficients, see Table 2.

Number	Reaction	Reaction rate
R1	$\text{O}_3 + h\nu \rightarrow \text{O}^{1\text{D}} + \text{O}_2$	$6.62 \times 10^{-5} \cdot e^{-\frac{0.575}{\cos(\chi)}}$
R2	$\text{O}^{1\text{D}} + \text{H}_2\text{O} \rightarrow \text{OH} + \text{OH}$	$1.63 \times 10^{-10} \cdot e^{\frac{60}{T}}$
R3	$\text{O}^{1\text{D}} + \text{N}_2 \rightarrow \text{O}_3$	$2.15 \times 10^{-11} \cdot e^{\frac{110}{T}}$
R4	$\text{O}^{1\text{D}} + \text{O}_2 \rightarrow \text{O}_3$	$3.30 \times 10^{-11} \cdot e^{\frac{55}{T}}$
R5	$\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}_3$	$1.67 \times 10^{-2} \cdot e^{-\frac{0.575}{\cos(\chi)}}$
R6	$\text{CH}_2\text{O} + h\nu \rightarrow \text{HO}_2$	$5.88 \times 10^{-5} \cdot e^{-\frac{0.575}{\cos(\chi)}}$
R7	$\text{OH} + \text{CO} \rightarrow \text{HO}_2 + \text{CO}_2$	2.40×10^{-13}
R8	$\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3\text{O}_2$	$2.45 \times 10^{-12} \cdot e^{-\frac{1775}{T}}$
R9	$\text{OH} + \text{ISO} \rightarrow \text{ISORO}_2$	1.00×10^{-10}
R10	$\text{OH} + \text{MVK} \rightarrow \text{HO}_2 + \text{CH}_2\text{O}$	2.40×10^{-11}
R11	$\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2$	$3.50 \times 10^{-12} \cdot e^{\frac{250}{T}}$
R12	$\text{CH}_3\text{O}_2 + \text{NO} \rightarrow \text{HO}_2 + \text{NO}_2 + \text{CH}_2\text{O}$	$2.80 \times 10^{-12} \cdot e^{\frac{300}{T}}$
R13	$\text{ISORO}_2 + \text{NO} \rightarrow \text{HO}_2 + \text{NO}_2 + \text{CH}_2\text{O} + \text{MVK}$	1.00×10^{-11}
R14	$\text{OH} + \text{CH}_2\text{O} \rightarrow \text{HO}_2$	$5.50 \times 10^{-12} \cdot e^{\frac{125}{T}}$
R15	$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2$	*
R16	$\text{CH}_3\text{O}_2 + \text{HO}_2 \rightarrow \text{PRODUCTS}$	$4.10 \times 10^{-13} \cdot e^{\frac{750}{T}}$
R17	$\text{ISORO}_2 + \text{HO}_2 \rightarrow n\text{OH} + \text{PRODUCTS}$	1.50×10^{-11}
R18	$\text{OH} + \text{NO}_2 \rightarrow \text{HNO}_3$	$3.50 \times 10^{-12} \cdot e^{\frac{340}{T}}$
R19	$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + (\text{O}_2)$	$3.00 \times 10^{-12} \cdot e^{-\frac{1500}{T}}$
R20	$\text{TERP} + \text{O}_3 \rightarrow \alpha_1\text{C}_1 + \alpha_2\text{C}_2 + \alpha_3\text{C}_3 + \alpha_4\text{C}_4$	$5.0 \times 10^{-16} \cdot e^{-\frac{530}{T}}$
R21	$\text{TERP} + \text{OH} \rightarrow \alpha_1\text{C}_1 + \alpha_2\text{C}_2 + \alpha_3\text{C}_3 + \alpha_4\text{C}_4$	$1.21 \times 10^{-11} \cdot e^{\frac{436}{T}}$

$$* k = (k_1 + k_2) \cdot k_3;$$

$$k_1 = 2.2 \times 10^{-13} \cdot e^{\frac{600}{T}};$$

$$k_2 = 1.91 \times 10^{-33} \cdot e^{\frac{980}{T}} \cdot c_{\text{air}};$$

$$k_3 = 1 + 1.4 \times 10^{-21} \cdot e^{\frac{2200}{T}} \cdot c_{\text{H}_2\text{O}}$$

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Table 2. Stoichiometric coefficients at $T = 298\text{K}$ for the different volatility bins, with saturation concentration C_i^* in $\mu\text{g m}^{-3}$ from Tsimpidi et al. (2010).

i	1	2	3	4
C_i^*	1	10	100	1000
α_i	0.107	0.092	0.359	0.600

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Table 3. VOC-emissions for the case study. Emissions during the day follow a sinus with the maximum emission flux ($\mu\text{g m}^{-2} \text{h}^{-1}$) as specified.

ISO	α -pinene	TERP
101	111	304

Table 4. The initial and boundary conditions in boundary layer (BL) and free troposphere (FT) as obtained from fitting MXLCH-SOA to the case study observations. All initial conditions are imposed at 07:50 LT. Heat fluxes are applied from 07:50 to 18:50 LT with $H = \rho c_p \overline{w'\theta'_s}$ and $LE = \rho L_v \overline{w'q'_s}$. t is the time (s) and t_d the length of the simulation (s). The subscripts s and e indicate values at the surface and the entrainment zone, respectively.

Property	Value
Initial BL height h (m)	200
Subsidence ω (s^{-1})	0
Surface sensible heat flux $\overline{w'\theta'_s}$ (Kms^{-1})	$0.11 \sin(\pi t/t_d)$
Entrainment/surface heat-flux ratio $\beta = -\overline{w'\theta'_e}/\overline{w'\theta'_s}$ (-)	0.2
Initial BL potential temperature $\langle \theta \rangle$ (K)	288
Initial FT potential temperature θ_{FT} (K)	288.4
Potential temperature lapse rate FT γ_θ (Km^{-1})	0.0035
Surface latent heat flux $\overline{w'q'_s}$ ($gkg^{-1}ms^{-1}$)	$0.06 \sin(\pi t/t_d)$
Initial BL specific humidity $\langle q \rangle$ (gkg^{-1})	8.0
Initial FT specific humidity q_{FT} (gkg^{-1})	6.25
Specific humidity lapse rate FT γ_θ ($gkg^{-1}m^{-1}$)	-0.0024

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Table 5. Initial mixing ratio in BL and FT and surface emission fluxes of the reactants as obtained from fitting MXLCH-SOA to the case study observations. Species in the reaction mechanism that are not included in this table have zero initial concentrations and zero surface emissions, except TERP and ISO (see Table 3). For the molecules O_2 and N_2 we have imposed the values 2×10^8 and 8×10^8 ppb, respectively.

	O_3	NO	NO_2	CH_4	CO
Initial mixing ratio (ppb)					
BL	31.0	0.04	0.1	1800.	100.
FT	39.0	0.0	0.2	1800.	100.
Surface emission flux ($ppb\,ms^{-1}$)	$-0.20 \sin\left(\frac{\pi t}{t_d}\right)$	4×10^{-3}	0.0	0.0	0.0

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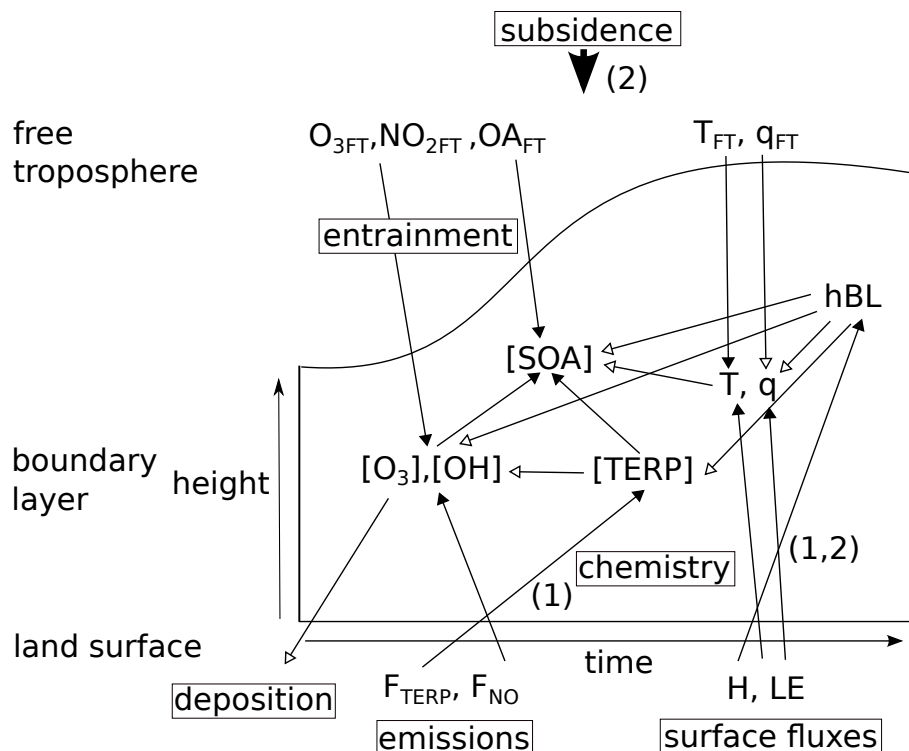


Fig. 1. Scheme of the interactions in and the boundaries of the system studied in this work. The numbers relate to the forcings of the system that are varied in the sensitivity analysis. Closed arrows indicate a positive relation, open arrows a negative relation and circles relations which can be either positive or negative. Processes are indicated in the boxes.

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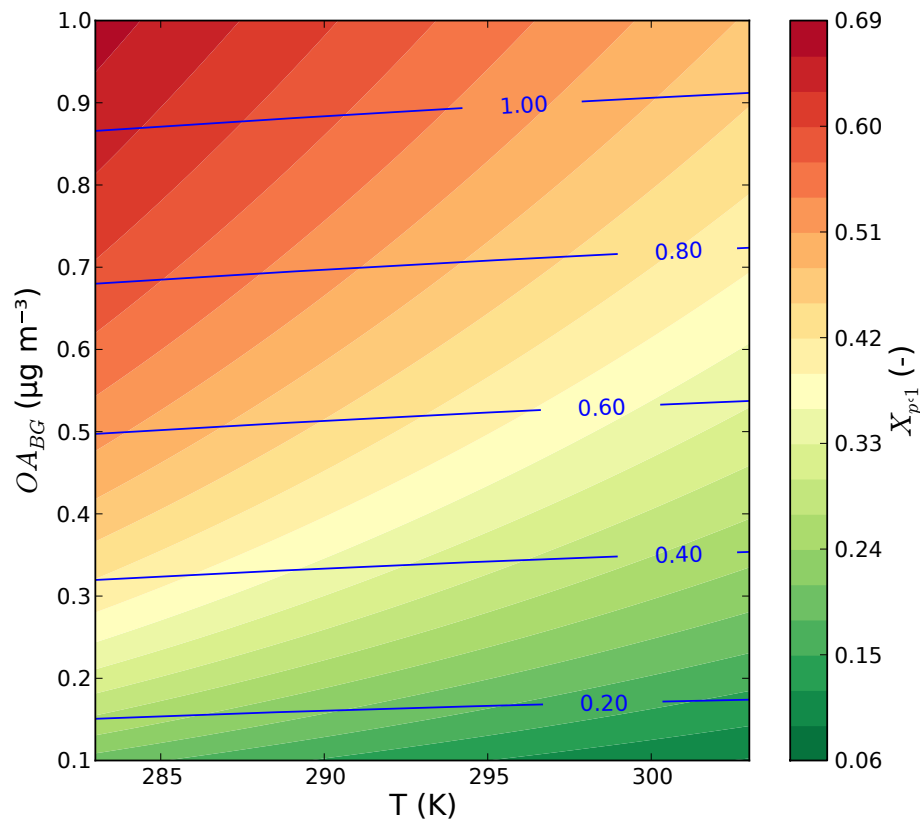


Fig. 2. Sensitivity of the partitioning coefficient of the first bin ($X_{p,1}$) and organic aerosol concentration (C_{OA}) to temperature (T) and the background organic aerosol concentration (OA_{BG}). Shades indicate $X_{p,1}$ (-) and the blue contours C_{OA} ($\mu\text{g m}^{-3}$).

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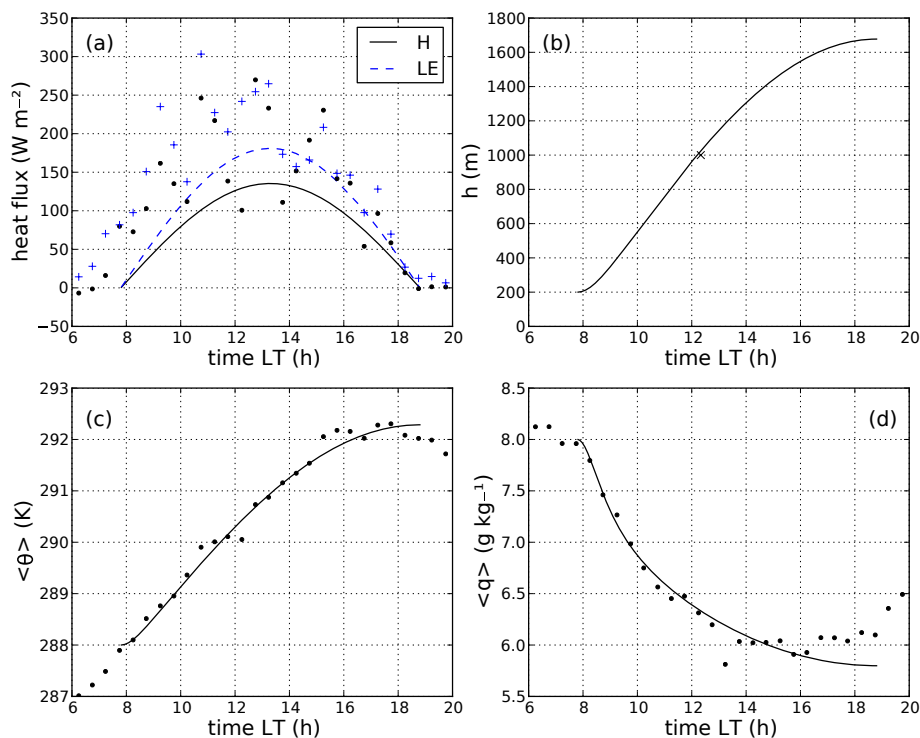


Fig. 3. Diurnal evolution of **(a)** surface sensible (H) and latent (LE) heat flux, which are both prescribed, **(b)** boundary layer height (h), **(c)** mixed layer potential temperature ($\langle \theta \rangle$) and **(d)** mixed layer specific moisture ($\langle q \rangle$) for the case study. Dots and crosses indicate tower (at 67.2 m) and balloon measurements, respectively. Model results are indicated by lines.

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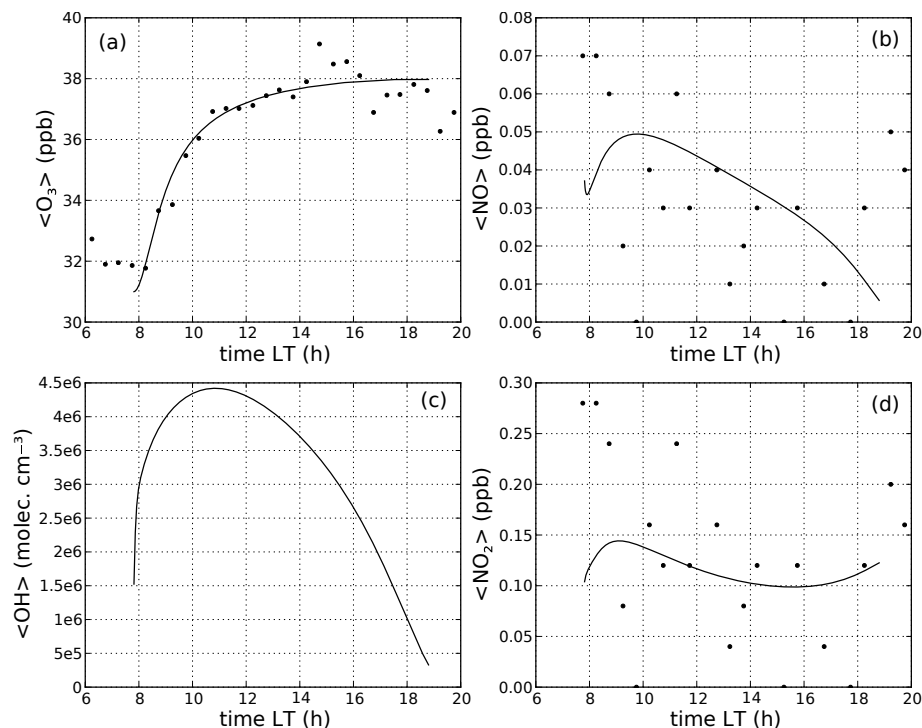


Fig. 4. Diurnal evolution of mixed layer concentrations of (a) O_3 , (b) NO , (c) OH and (d) NO_2 for the case study. NO_2 -measurements are scaled down to match the NO_2/NO -ratio of 5 as obtained during summer 2010 from more reliable measurements than those from August 2001. Dots indicate measurements from the tower at 67.2 m. Model results are indicated by lines.

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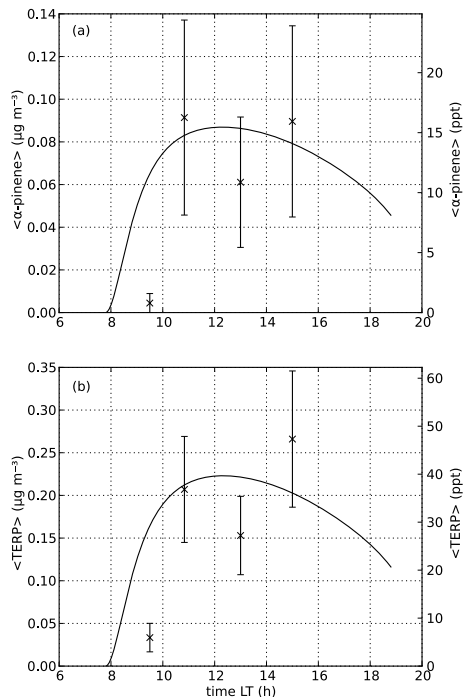


Fig. 5. (a) (α -pinene) and **(b)** sum of terpenes (\langle TERP \rangle) for the case study. Crosses indicate balloon measurements and model results are indicated by lines. Errors are 100 % for concentrations lower than $0.03 \mu\text{g m}^{-3}$, 50 % for concentrations between 0.03 and $0.15 \mu\text{g m}^{-3}$ and 30 % for concentrations higher than $0.15 \mu\text{g m}^{-3}$. The conversion factor from $\mu\text{g m}^{-3}$ to ppt is 178.

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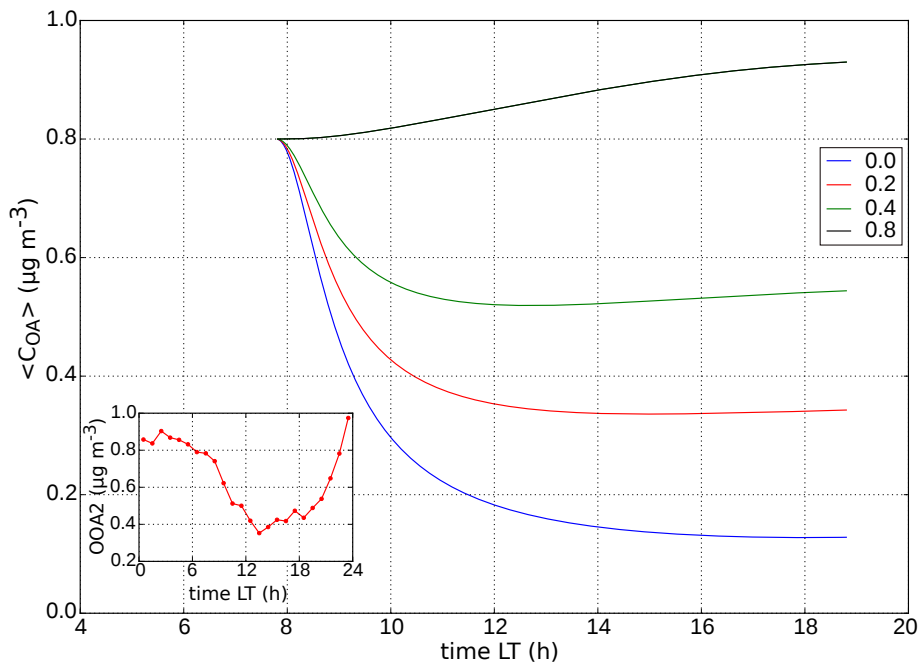


Fig. 6. Organic aerosol concentration C_{OA} for the case study, including the sensitivity to different FT background OA-concentrations (0.0, 0.2, 0.4, 0.8 $\mu\text{g m}^{-3}$). The inset shows the diurnal cycle of the measured OOA2-concentration, averaged over 15 days.

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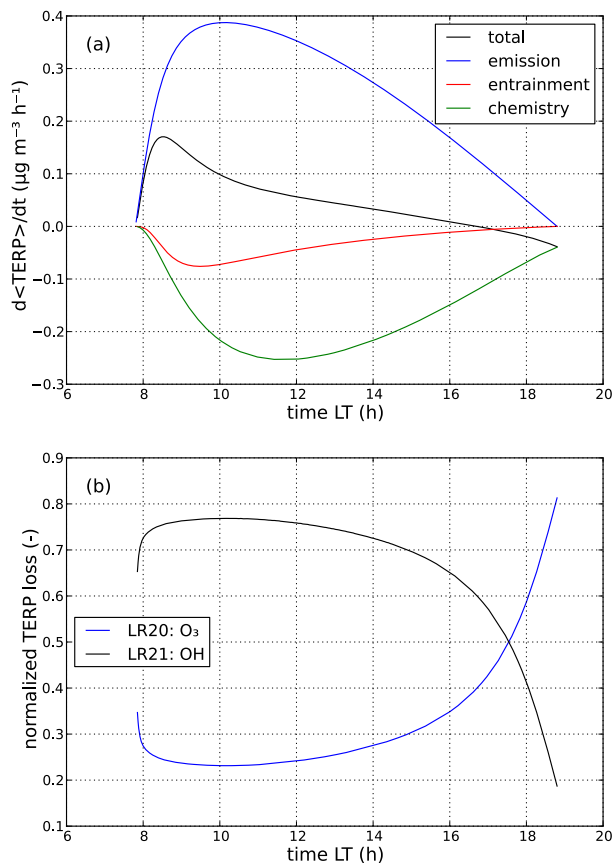


Fig. 7. Contribution of the individual processes to the terpene tendency for the case study. **(a)** total tendency and the individual contributions of emission, entrainment and chemistry and **(b)** the normalized contribution to the chemical terpene loss of the reaction with O₃ and OH.

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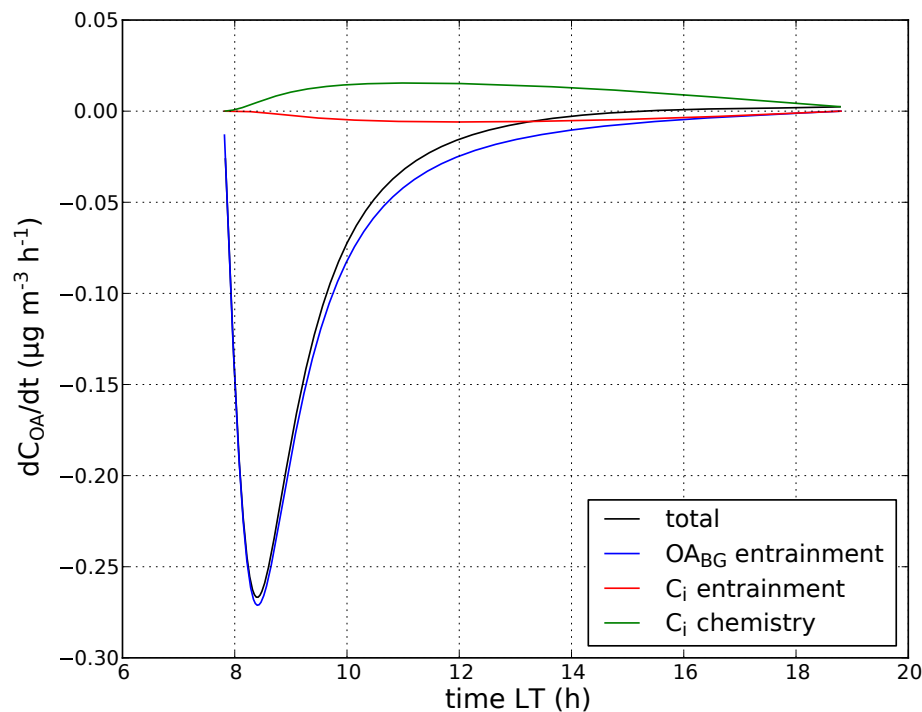


Fig. 8. Organic aerosol tendency for the case study. Shown are the total tendency and the contributions of the entrainment of background organic aerosol (OA_{BG}), the entrainment of condensable products from terpene oxidation (C_i) and the chemical production of C_i to the tendency.

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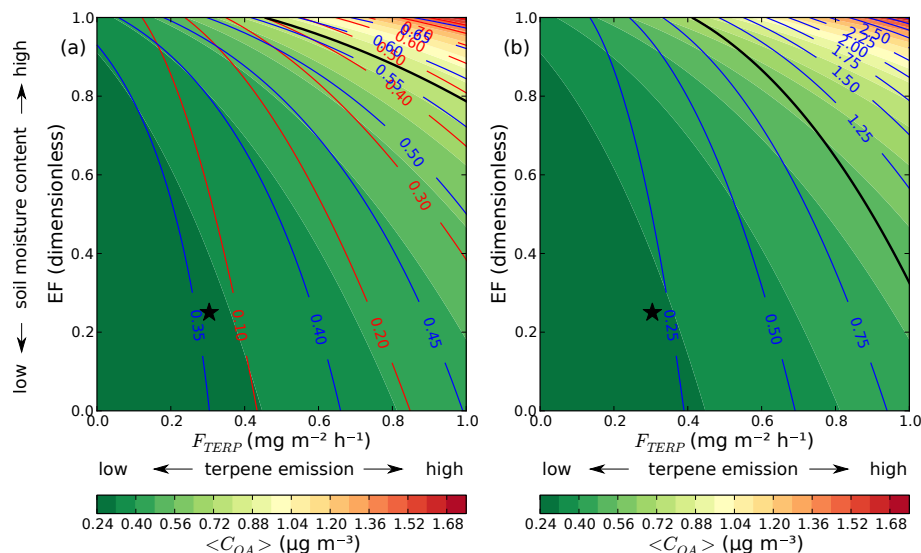


Fig. 9. (a) Sensitivity of organic aerosol concentration C_{OA} and TERP-concentration at 18:50 LT to terpene emission (F_{TERP}) and evaporative fraction (EF). Shades indicate organic aerosol concentration C_{OA} ($\mu\text{g m}^{-3}$), the red contours the TERP-concentration ($\mu\text{g m}^{-3}$) and the blue contours the partitioning coefficient $X_{p,1}$. The black contour indicates the conditions for which the C_{OA} at the end of the day equals the initial concentration and the asterisk indicates the conditions for the case study. (b) Sensitivity of organic aerosol concentration C_{OA} and the OA chemistry-background ratio r_{FB} at 18:50 LT to F_{TERP} and EF. Shades indicate C_{OA} ($\mu\text{g m}^{-3}$) and the blue contours r_{FB} . The black contour indicates the conditions for which the C_{OA} consists of equal parts of OA_{TERP} and OA_{BG} ($r_{FB} = 1$) and the asterisk indicates the conditions for the case study.

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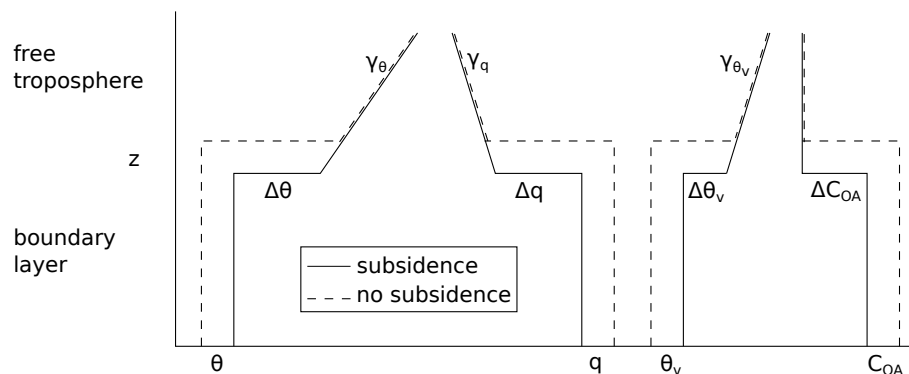


Fig. 10. Sketches of the vertical profiles of θ , q , θ_v and C_{OA} at the end of the day (18:50), in case of subsidence and no subsidence, respectively. A Δ indicates the jump of a scalar or reactant C defined as $\Delta C = C_{\text{FT}} - \langle C \rangle$ and a γ_C the lapse rate of a scalar C in the FT.

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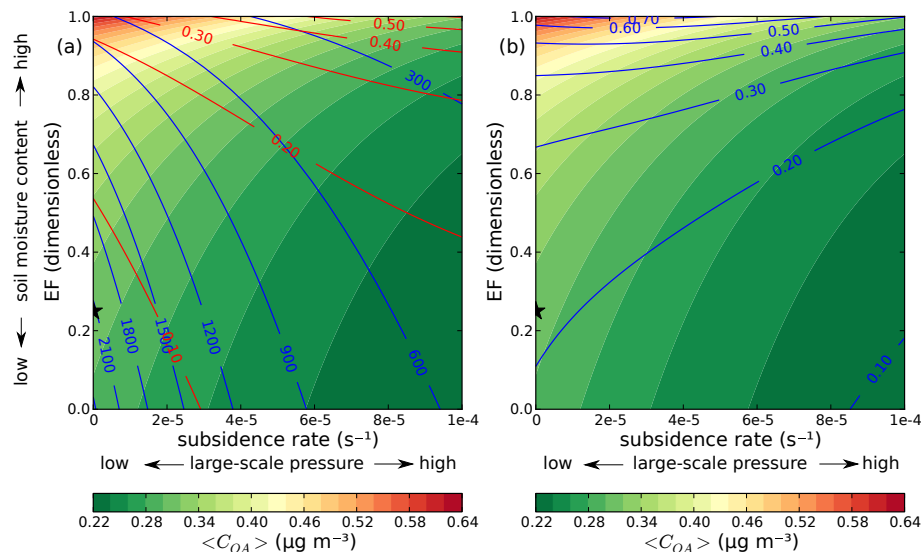


Fig. 11. (a) Sensitivity of organic aerosol concentration (C_{OA}), BL-height (h) and TERP-concentration at 18:50 LT to subsidence and evaporative fraction (EF). Shades indicate C_{OA} ($\mu g m^{-3}$), the blue contours h (m) and the red contours TERP-concentration ($\mu g m^{-3}$). (b) Sensitivity of C_{OA} and the the OA chemistry-background ratio (r_{FB}) at 18:50 LT to subsidence and evaporative fraction (EF). Shades indicate C_{OA} ($\mu g m^{-3}$) and the blue contours r_{FB} ($-$). The asterisk indicates the conditions for the case study.

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