Study of the diurnal variability of atmospheric chemistry with respect to boundary layer dynamics during DOMINO

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Abstract

We study the interactions between atmospheric boundary layer (ABL) dynamics and atmospheric chemistry using a mixed-layer model (MXLCH) coupled to chemical reaction schemes. Guided by both atmospheric and chemical measurements obtained during the DOMINO campaign (2008), numerical experiments are performed to study the role of ABL dynamics and the accuracy of chemical schemes with different complexity: MOZART-4 and a reduced mechanism of this chemical system. Both schemes produce satisfactory results, indicating that the reduced scheme is capable of reproducing the \( \text{O}_3\)-\( \text{NO}_x\)-\( \text{VOC}\)-\( \text{HO}_x \) diurnal cycle during conditions characterised by a low \( \text{NO}_x \) regime and small \( \text{O}_3 \) tendencies (less than 1 ppb per hour). By focussing on the budget equations of chemical species in the mixed-layer model, we show that for species like \( \text{O}_3 \), \( \text{NO} \) and \( \text{NO}_2 \), the influence of entrainment and boundary layer growth is of the same order as chemical production/loss. This indicates that an accurate representation of ABL processes is crucial in understanding the daily cycle of chemical species. By comparing the time scales of chemical reactive species with the mixing time scale of turbulence, we propose a classification based on the Damköhler number to further determine the importance of dynamics on chemistry during field campaigns. Our findings advocate an integrated approach, simultaneously solving the ABL dynamics and chemical reactions, in order to obtain a better understanding of chemical pathways and processes and the interpretation of the results obtained during measurement campaigns.

1 Introduction

Present day research on atmospheric chemistry covers a vast range of scales and approaches. Focusing on isoprene, there are for instance highly fundamental studies, either based on a theoretical approach (Peeters et al., 2009) or on small scale laboratory experiments in reaction chambers (Paulot et al., 2009), and studies with a more...
applied approach. Examples of the latter are controlled experiments in box models (Sander et al., 2011) and simulations at a global scale using global transport models (Stavrakou et al., 2010). However, in order to obtain a better understanding of the chemical system in real-life conditions, field experiments like e.g. TROFEE (Yokelson et al., 2007), DOMINO (Sörgel et al., 2011; Crowley et al., 2011; Diesch et al., 2011) and HUMPPA-COPEC (Williams et al., 2011) are conducted, the majority of which are strongly modulated by the diel variability of the atmospheric boundary layer (ABL). This adds further complexity to the interpretation of the data, which is often undervalued. Here, in analysing the diurnal variability of the reactants during DOMINO, we propose an integrated approach, simultaneously solving the ABL development and chemical transformation within a conceptual meteorological model in order to obtain a better understanding and representation of the daily cycle of chemical species.

The temporal evolution of atmospheric chemistry is controlled by both chemical processes and the development of the ABL (Ganzeveld et al., 2008; Vilà-Guerau de Arel-lano et al., 2011). Especially for convective cases characterised by a strong diel cy-cle, the influence of boundary layer growth and entrainment plays a crucial role in the diurnal cycle of atmospheric chemical species. As the influence of boundary layer dynamics acts on similar time-scales (∼30 min) as certain chemical transformations, dynamics and chemistry have to be addressed as an integrated whole.

In this paper we systematically study the effect of boundary layer dynamics on atmos-pheric chemistry by quantifying their respective influence by means of a mixed-layer model coupled to a chemical reaction scheme. Under diurnal conditions, mixed-layer theory is a satisfactory compromise between a box model (no characterization of ABL dynamics) and more advanced 3-D (large-eddy simulation, mesoscale or global circu-lation) models. The simplicity of the mixed-layer model enables us to obtain insight on the underlying processes and is very suitable/complementary for the interpretation of measurement campaigns. More specifically, we use one day during the DOMINO (Diel Oxidant Mechanisms in relation to Nitrogen Oxides) measurement campaign, conducted in November 2008 near Mazagón, south western Spain. The campaign
focussed on the diel cycle of chemistry in relation to meteorology, combining the measurement of chemical species with meteorological surface and upper air observations. With (amongst others) ozone, nitrogen oxides and vertical profiles of temperature and moisture, the dataset provides a unique opportunity to comprehensively study and validate the interplay between the dynamics and atmospheric chemistry in the ABL.

Using the measurement data, we reproduce the boundary layer development of a single day during DOMINO with the mixed-layer model. Two different reaction schemes are integrated in the mixed-layer model: the Model for Ozone and Related chemical Tracers, version 4 (MOZART-4, hereafter: MOZART) (Emmons et al., 2010) and an extended version of the reaction schemes used by Vilà-Guerau de Arellano et al. (2009, 2011) and Ouwersloot et al. (2011). The latter consists of a reduced mechanism of the chemical system. In absence of a complete set of measurements, this minimizes the assumptions made in the initial and boundary conditions, like e.g. the initial mixing ratios or surface emissions or deposition.

Our main objectives are: (1) to quantify the influence of boundary layer dynamics on atmospheric chemistry, (2) to show the benefits in using conceptual models as a method to obtain a better understanding and complementary information of measured data and (3) to discuss the current state of the art of modelling, comparing the complex MOZART chemical scheme with a simplified reaction scheme.

Our research approach and structure of the article is as follows: we start in Sect. 2 with a short description of the mixed-layer model and chemical reaction schemes. In Sect. 3 the large scale atmospheric synoptic and boundary layer dynamics of the studied day are addressed, followed by the design of the numerical experiments. In Sect. 4 we discuss the modelled results, comparing MOZART and the reduced scheme with measurements. Next, we examine the budget equations of chemical species, separating the influence of boundary layer dynamics (entrainment and boundary layer growth) from the contributions of other processes like surface emission/deposition or chemical transformations. This allows us to study the relative importance of boundary layer dynamics compared to chemical reactions. This is further supported by studying the
characteristic time scales of chemistry and turbulence as an appropriate indicator of the
development of the relevance of chemistry versus dynamics for fast and slow reacting chemical species.
In Sect. 5 we conclude the paper by summarizing the main conclusions.

2 Mixed-layer model

2.1 Representation boundary layer dynamics

The MiXed Layer CHemistry (MXLCH) model stems from the pioneering research of
Lilly (1968); Betts (1973); Tennekes and Driedonks (1981) on the dynamics of clear
and cloudy boundary layers. In short, the model solves the time development of idealized
vertical profiles of dynamic variables (potential temperature ($\theta$), specific humidity ($q$)) and chemical species ($S$) like nitrogen dioxide ($NO_2$) or ozone ($O_3$). As shown
schematically in Fig. 1, the mixed-layer quantities are expected to be perfectly mixed
by turbulence. Consequently, we can define the mixed-layer variables to be constant
with height:

$$\langle \phi \rangle = \frac{1}{h} \int_s^h \phi(z) \, dz,$$

with $\phi = \{\theta, q, S\}$ and “$s$” and “$h$” denote the surface and mixed-layer height. The equations governing $\langle \phi \rangle$ are derived by vertically integrating the one dimensional Reynolds averaged Navier-Stokes equations, resulting in:

$$\frac{\partial \langle \phi \rangle}{\partial t} = \frac{w' \phi'_s - w' \phi'_h}{h} + S_\phi.$$

Here $w' \phi'$ denotes a turbulent flux and $S_\phi$ contains additional source and sink terms, for chemical species the production and/or loss rates in chemical reactions. An additional term for advection has been omitted, but can easily be included in a similar manner like $S_\phi$. The mixed-layer top discontinuity $\Delta \phi$, marking the interface between
the unstable mixed-layer and stable free troposphere, evolves in time as the combined result of mixed-layer growth and changes in the bulk quantity:

\[
\frac{\partial \Delta \phi}{\partial t} = \frac{\partial \phi_{\text{FT}}}{\partial t} - \frac{\partial \langle \phi \rangle}{\partial t} = \gamma \phi \left( \frac{\partial h}{\partial t} - w_s \right) - \frac{\partial \langle \phi \rangle}{\partial t},
\]

where \( \phi_{\text{FT}} \) and \( \gamma \phi \) represent respectively the condition directly above the inversion and the free tropospheric lapse rate (Fig. 1). The mixed-layer grows due to entrainment, opposed by large scale vertical motions:

\[
\frac{\partial h}{\partial t} = w_e + w_s,
\]

where \( w_e \) and \( w_s \) represent the entrainment and subsidence velocity, the latter is defined as \( w_s = (\nabla \times \mathbf{v}_h) \cdot h \) with \( \nabla \times \mathbf{v}_h \) the horizontal velocity divergence. The entrainment velocity is calculated as:

\[
w_e = \frac{-w'\theta'_{v;h}}{\Delta \theta_v}.
\]

Note that virtual temperatures are used to include the influence of moisture on buoyancy (Stull, 1988). In order to close this set of equations, the entrainment flux of (virtual) heat is parametrized as a negative fixed fraction (\( \beta \)) of the surface heat flux:

\[
w'_\theta'_{v;h} = -\beta w'_\theta'_{v;s},
\]

and written into Eq. (5). This relates the entrainment of not only heat, but also moisture and chemical species to the surface flux of heat and the thermodynamic structure as \( w_e \) is used to calculate the entrainment fluxes:

\[
w'_\phi'_{h} = -w_e \Delta \phi.
\]

Buoyancy (mainly controlled by heat) is therefore a key variable, actively influencing the budgets of chemical reactive species. Explained in words, the tendencies of heat,
moisture and chemical species depend on the mixing of any input at the surface (latent and sensible heat fluxes and, for chemical species, the emission or deposition fluxes) and the entrained air from the free troposphere over the mixed-layer depth. Depending on the sign of $\Delta \phi$ and therefore the difference between the mixed-layer and free troposphere, the influence of entrainment on the budget of a chemical species can be negative or positive. For instance, for the examples shown in Fig. 1, entrainment will decrease $\langle \text{NO}_2 \rangle$ as air with a lower mixing ratio is entrained into the mixed-layer. For $\text{O}_3$, the opposite occurs and entrainment will increase $\langle \text{O}_3 \rangle$.

### 2.2 Representation of chemistry

As a representation for the chemical reactions, two chemical reaction schemes are implemented in MXLCH: MOZART (Emmons et al., 2010) and an extended version of the reaction schemes used by Vilà-Guerau de Arellano et al. (2009, 2011); Ouwersloot et al. (2011), where the latter consists of a reduced mechanism of the chemical system. Despite being less complete in both the number of chemical species and reaction equations, the reduced scheme has a number of advantages over MOZART:

1. As the scheme contains less species and equations, the computational costs are minimized while the scheme still retains the essential components of the $\text{O}_3$-$\text{NO}_x$-$\text{VOC}$-$\text{HO}_x$ cycle (Vilà-Guerau de Arellano et al., 2011). Although computational time is no limiting factor when using a conceptual model like MXLCH, use of the reduced scheme can act as a validation before implementing it in for instance large-eddy simulation (e.g. Ouwersloot et al., 2011) where the number of reactions does put a serious constraint on the computational possibilities.

2. Using a limited number of species and reactions, the chemical system remains tractable, resulting in a better understanding of the main underlying chemical pathways.
3. By including less species, the degrees of freedom are reduced, resulting in less uncertainty in the initialisation and boundary conditions (emission/deposition variability and initial properties of the mixed-layer and free troposphere) of the model. The chemical reactions employed in the reduced scheme are presented in Table 1. The reaction rate coefficients are from the International Union of Pure and Applied Chemistry (IUPAC), Subcommittee for Gas Kinetic Data Evaluation (http://www.iupac-kinetic.ch.cam.ac.uk/) All chemical reactions are solved at each time step of $dt = 1 \text{s}$ for both the mixed-layer and free troposphere.

### 3 Case description

Our numerical experiments are based on measurement data obtained during the DOMINO campaign, conducted at the Atmospheric Sounding Station – El Arenosillo (37.1° N, 6.7° W, +40 m a.m.s.l.), a platform of the Atmospheric Research and Instrumentation Branch of the Spanish National Institute for Aerospace Technology (INTA), dedicated to atmospheric measurements in the Southwest of Spain. From this dataset, we selected the 23 November 2008 as it was an ideal day; characterized by a relative small influence of large synoptic scales and with lower build up of ozone (less than 10 ppb in 10 h). Furthermore, this day was in an intense observation period with high frequency balloon soundings (hourly, measuring the location, temperature, humidity and pressure) and comprehensive coverage of the chemical measurements. With high pressure over Spain (Azores High), it was a cloudless day with a moderate (1–4 m s$^{-1}$) NNE flow in which an initially shallow stable boundary layer developed into a convective boundary layer with a depth of approximately 1400 m at 15:00 UTC. Figure 2 shows eight forward trajectories computed with the NOAA HYSPLIT model (Draxler and Rolph, 2011) using NCEP-GDAS as meteorological input files with $1° \times 1°$ spatial resolution. The trajectories were calculated in the ABL (near surface, 100 m) and free troposphere (2000 m), starting at the city of Sevilla and the industrial area near Huelva (petrochemical industry) at 08:00 UTC (ending at 13:00 UTC) and 12:00 UTC (ending...
at 17:00 UTC). In spite of the low resolution, the trajectories indicate that relative clean air was advected from these areas during 23 November. This is further corroborated by the relative low NO$_x$ and O$_3$ observations in Fig. 4. This ensures that the evolution in the observational chemical data is mainly controlled by local meteorological events: emission or deposition, chemical reactions or boundary layer dynamics, rather than transport.

The initial and boundary conditions used in MLXCH are presented in Tables 2 and 4. The initial temperature and moisture profiles are based on the atmospheric soundings and meteorological data measured at 50 m a.g.l. from a tall tower (100 m) available at El Arenosillo. As no measurements of the surface heat and moisture fluxes are available, we impose typical values given the location and time of the year. In addition to the experiments with MXLCH, a second experiment is conducted with a box model to provide a first quantification of the influence of ABL dynamics. With both the sensible and latent heat flux set to zero, MXLCH behaves as a box model with a fixed height, temperature and moisture content and no entrainment. The different experiments are summarized in Table 3. The initial mixed-layer and free tropospheric mixing ratios and surface forcings (emission/deposition) of chemical species are shown in Table 4. The initial mixing ratios are based on the DOMINO measurements. All other species (except for molecular oxygen and nitrogen) are initialized at zero.

4 Results

4.1 Temporal evolution dynamics and chemistry

The temporal evolution of the mixed-layer height ($h$) and slab averaged potential temperature ($\theta$) and specific humidity ($q$) is shown in Fig. 3a–c. When around 09:00 UTC the surface sensible heat flux has broken the ground inversion by heating the ABL, the mixed-layer encounters a rapid growth of approximately 200 m h$^{-1}$ between 09:00 UTC and 12:00 UTC. As the mixed-layer grows, air with properties of the free troposphere...
is entrained into the mixed-layer, causing an increase in potential temperature (en-
trainment of relative warm air) and decrease in specific humidity (entrainment of dry
air). Comparison with the measurements show that the mixed-layer model correctly
represents the dynamical evolution of the ABL. Subsidence (Eq. 4, Table 2) plays a
relatively small role and decreases the mixed-layer growth with 200 m throughout the
day. Especially the accurate representation of the mixed-layer height is crucial for the
budgets of chemical species, not only because of its influence on entrainment, but also
as $h$ is the mixing-depth of any input or loss at the surface or mixed-layer top (Eq. 2).
This encourages frequent probing of the atmosphere (like e.g. during DOMINO with
balloon soundings at a 1 h interval) as the mixed-layer height is calculated as the maxi-
imum temperature gradient of the upper air soundings, and frequent measurements are
needed to capture the rapid development in the early morning. In addition to the ther-
modynamic variables, we show in Fig. 3d the photolysis rate of NO$_2$, a quantity driven
by ultraviolet radiation. To calculate the photolysis rate of NO$_2$, we use the empirical
expression of Wiegand and Bofinger (2000). Both MOZART and the reduced scheme
correctly reproduce the measured photolysis rate of NO$_2$ and in addition (not shown),
produce similar results as the TUV model (Madronich et al., 2011) for the photolysis
rates of O$_3$ and CH$_2$O.

Figure 4 shows the diurnal variation of O$_3$, NO, NO$_2$ and HNO$_3$. Although the ten-
dencies are similar, the results obtained with experiment BOX750 tend to overestimate
the mixing ratio evolution. This is the combined effect of not taking mixed-layer growth
and entrainment, the exchange between the ABL and free troposphere, into account.
MXLCH with both MOZART and the reduced scheme is capable of reproducing the
measured mixing ratios. The mixing ratio of O$_3$ is slightly underestimated with MOZART
and NO$_2$ slightly overestimated using the reduced chemistry scheme. In spite of being
a reduced scheme, the scheme presented in Table 1 is able to reproduce the observ-
ational trend of O$_3$, NO and NO$_2$ and same characteristic ratios like NO$_2$/NO $\approx$ 2–3.
This indicates that in regimes where ozone increases smoothly, the scheme performs
satisfactorily. Also, given the differences between the observations, the box model and
MXLCH with both reaction schemes, it needs to be stressed that ABL dynamics plays a key role in reproducing and understanding the measured mixing ratios.

The satisfactory results of the reduced scheme are further corroborated by the inter-comparison of isoprene, OH, HO$_2$ and H$_2$O$_2$ in Fig. 5. For isoprene, MOZART and the reduced scheme both have different tendencies compared with the few observations, but the mixing ratios are of a similar order. For OH, HO$_2$ and H$_2$O$_2$, both MOZART and the reduced scheme are close to the measured data where, on average, MOZART underestimates the mixing ratios due to the introduction of additional reactions that destroy OH. However, the measured OH mixing-ratios are upper-limit values, possibly overestimating the mixing ratio by up to a factor two (Sörgel et al., 2011). It should also be mentioned that although we are not accounting for key chemical pathways like the formation of OH from HONO (Sörgel et al., 2011), our findings provide a comprehensible evolution of reactants in the ABL. In this respect, although we are missing details near the surface (an example is given in Fig. 3 of Vilà-Guerau de Arellano et al. (2011)), we take advantage of the rapid mixing efficiency of the ABL, driven by convective turbulence.

4.2 Budgeting of chemical reactants

MXLCH enables us to further determine the individual contributions of emission/deposition, chemical transformation and entrainment to the evolution of the (reactive) species, i.e. the different terms of Eq. (2). We selected four species to examine the variation in time of the contribution of both dynamics and chemistry. The dynamic part is here defined as the mixing of both surface emissions/deposition and the entrained air over the mixed-layer depth $h$ whereas the chemical contribution is the net production or loss rate from the equations in Table 1:
\[
\frac{\partial \langle S \rangle}{\partial t} = \frac{Ds}{h} - \frac{De}{h} + \frac{Cp}{h} \langle S \rangle_{\text{prod}} - \langle S \rangle_{\text{loss}}.
\]

(8)

Figure 6 shows the budgets of O\(_3\), NO, NO\(_2\) and OH. As Fig. 6a shows, the net \(\text{O}_3\) tendency is positive throughout almost the entire day (see Fig. 4a) with a maximum increase in \(\text{O}_3\) around 09:30 UTC. The peak is closely related to the maximum in entrainment (\(D_e\)) of ozone originating in the free troposphere, at this time caused by (1) the rapid growing mixed-layer (Fig. 3) and (2) the relative large difference in mixing ratio between the mixed-layer and free troposphere (\(\Delta \text{O}_3 \approx 7\) ppb). When during the day the \(\text{O}_3\) mixing ratio increases (decreasing \(\Delta \text{O}_3\) towards zero) and the mixed-layer growth decreases, the contribution of entrainment relative to the chemical term decreases to zero around 14:00 UTC. From 08:00 UTC onwards the net chemical tendency is positive and equals the contribution by entrainment around 11:00 UTC. After \(\sim 13:00\) UTC the total ozone tendency is mainly driven by chemical reactions. This makes that the total \(\text{O}_3\) tendency is mainly controlled by dynamics during the morning growth of the ABL and by chemistry in the afternoon.

The tendency of NO, shown in Fig. 6b, is positive up to 09:30 UTC and negative afterwards, in agreement with the peak observed in Fig. 4b. Since the initial mixing ratios and thus initial \(\Delta \text{NO}\) is zero, the relative contribution of entrainment to the total tendency is small. Only when the mixed-layer mixing ratio has increased towards its maximum around 10:00 UTC, growth of the mixed-layer causes entrainment of air with a relative low mixing ratio (\(\Delta \text{NO} \approx -0.14\) ppb), resulting in a small (negative) contribution to the total tendency. The total tendency is therefore the result of a balance between the surface emission and the net chemical loss. Despite being forced with a fixed surface emission (Table 4), \(Ds\) decreases throughout the day as the mixed-layer grows, because this term is inversely proportional to \(h\) (see Eq. 8). This demonstrates
that, without having a strong influence of entrainment, ABL dynamics still influences the tendencies of chemical species, as shown by the first RHS term of Eq. (8).

Figure 6c shows the budget of NO$_2$. With a lower mixing ratio in the free troposphere, entrainment results in a decrease of NO$_2$ which, like for ozone, is the strongest around 09:30 UTC. At the same time, deposition causes an extra loss of NO$_2$. With the deposition calculated as $-\nu_c C_{NO_2}$ with $\nu_c$ constant (Table 4), the contribution of deposition decreases as both the NO$_2$ mixing ratio decreases and the mixed-layer grows. Combined, the dynamical contribution causes a strong negative tendency during the day. Chemical transformations counter the dynamical contribution. However only during the morning (when the contribution of entrainment is still small) and late afternoon (when the mixed-layer reaches its maximum height) the net chemical production is sufficient to create a net positive tendency of NO$_2$.

For faster reacting species like OH in Fig. 6d, the tendency is mostly controlled by chemical production and loss. This indicates that, for species with a short lifetime or high reactivity, the chemical part of Eq. (8) dominates and the influence of ABL dynamics decreases. This subject will be studied in more detail in the next section.

### 4.3 Time scales of turbulence and chemistry

To further substantiate the relative influence of mixed-layer dynamics compared to chemistry, and to provide a more robust quantification of the relative importance, we examine further the diurnal variability in terms of the characteristic time scales on which the different species and turbulence are acting. The Damköhler number (Damköhler, 1940), for mixing at large scales defined as the ratio of the typical turbulence time scale to the time scale of chemistry (Vilà-Guerau de Arellano, 2003), is the key dimensionless number to distinguish the influence of turbulence from chemistry:

$$Da = \frac{\tau_t}{\tau_{c,S}}; \tau_t = \frac{h}{w^*}; \tau_{c,S} = \frac{c_0}{C_l},$$  

(9)
with \( \tau_t \) the time scale of turbulence, \( \tau_{c:S} \) the time scale of chemical species \( S \), \( c_S \) the concentration of species \( S \) and \( C_l \) the chemical loss rate of species \( S \). \( w_* \) is the convective velocity scale, defined as (Stull, 1988):

\[
\begin{align*}
  w_* &= \sqrt{ \frac{3 g h \langle w' \theta'_v \rangle_{v:S}}{\langle \theta_v \rangle} }, \\
  \tau_t &= \frac{3}{w_*} \\
  \tau_{c:S} &= \frac{3}{c_S w_*} \\
  c_l &= \frac{3}{C_l w_*}
\end{align*}
\]

where \( g \) is the gravitational acceleration. The time scale \( \tau_t \) thus increases as the mixed-layer grows, while a stronger virtual heat flux \( \langle w' \theta'_v \rangle_{v:S} \) enhances turbulent mixing and therefore decreases the time scale. Based on the Damköhler number we can define the following regimes:

- \( Da_S \lesssim 0.1 \) – Slow chemistry where the mixing ratio is controlled by emission/deposition and ABL dynamics
- \( 0.1 \lesssim Da_S \lesssim 10 \) – Moderate chemistry where the mixing ratio is governed by ABL dynamics and chemical reactions
- \( Da_S \gtrsim 10 \) – Fast chemistry where the mixing ratio is determined by chemical reactions.

Under the regime of a Damköhler number \( Da_S \gtrsim 10 \), the influence of ABL dynamics is negligible for this chemical species and Eq. (8) reduces to only the chemical contributions. In contrast, a small Damköhler number of \( Da_S \lesssim 0.1 \) indicates an atmospheric reactive flow where the contribution of chemical reactions is relatively small compared to ABL dynamics or large scale forcings. For \( 0.1 \lesssim Da_S \lesssim 10 \) chemistry and dynamics interact and both the dynamical and chemical term of Eq. (8) needs to be taken into account. Using MXLCH, we are able to calculate the time scales of turbulence and the individual chemical species and as such provide an indicator for the relative importance of dynamics and chemistry.

Figure 7 shows the time scale \( \tau \) for both the convective ABL (“turbulence”) and a number of fast and slow reaction species. For the analysed day during DOMINO the
time scale of the ABL increases from \(\sim 400\) s at 09:00 UTC to \(\sim 1000\) s at 16:00 UTC. CO, here the slowest reacting species, acts on a time scale in the order of 10 days, resulting in a \(Da_S \ll 0.1\), indicating that CO for example is mainly controlled by atmospheric turbulence and transport. In contrast, OH, acts on a time scale of seconds or less, resulting in \(Da_S \gg 10\). This confirms the findings of Fig. 6d, where the OH budget was mainly determined by the chemical transformations. Closely connected with the chemical lifetime of OH is the OH-reactivity; the inverse of the lifetime (e.g. Di Carlo et al., 2004; Lelieveld et al., 2008; Sinha et al., 2008). During DOMINO, the reactivity of OH was directly measured with at 23 November values in the order of \(40 \text{s}^{-1}\) (Sinha et al., 2012). With average reactivities of \(1.4 \text{s}^{-1}\) (reduced scheme) and \(2 \text{s}^{-1}\) (MOZART), MXLCH underestimates the reactivity. As the modelled OH mixing ratio fits well to the measurements (Fig. 5), this indicates that both chemical schemes are missing chemical pathways related to the production and destruction of OH. This is still an open issue, possibly caused by an incomplete initialization of anthropogenic volatile organic compounds (VOC). Intermediate species like \(\text{O}_3\), \(\text{NO}\) and \(\text{NO}_2\) act on a time scale of minutes to hours, within \(\pm\) one order of magnitude of the typical time scale of the ABL, again corroborating the need to take dynamics and chemical transformations simultaneously into account.

5 Conclusions

In this study we used a mixed-layer model coupled to chemical reaction schemes to systematically study the influence of atmospheric boundary layer (ABL) dynamics on the time evolution of chemistry. We selected one day during the DOMINO measurement campaign and designed numerical experiments to determine the performance of two chemical schemes with different complexity (MOZART-4 and a reduced mechanism of this chemical system) under realistic dynamical conditions. Additional experiments with a box model, which neglects the influence ABL dynamics, display an overestimation in the mixing ratios of chemical species. The mixed-layer model with
both MOZART and the reduced reaction scheme performs satisfactory, reproducing
the measured mixing ratios of key chemical species like \( \text{O}_3 \) and \( \text{NO}_x \). This indicates
that, in conditions characterized by a low \( \text{NO}_x \) regime and small \( \text{O}_3 \) tendencies, the
reduced scheme is capable of reproducing the \( \text{O}_3 \)-\( \text{NO}_x \)-VOC-\( \text{HO}_x \) diurnal cycle. Under
these conditions, the reduced scheme is a useful, more comprehensible and computa-
tionally less expensive alternative for complex schemes like MOZART, for e.g. use in
large-eddy simulation.

By studying the individual contribution of emission/deposition, chemical transforma-
tion, mixed-layer growth and entrainment to the evolution of the reactive species, it is
found that for species like \( \text{O}_3 \), \( \text{NO} \), \( \text{NO}_2 \), the contribution of boundary layer processes
is of the same order as the contribution of chemical transformations. Both \( \text{O}_3 \) and \( \text{NO}_2 \)
are strongly controlled by entrainment of relatively ozone rich and nitrogen dioxide poor
air originated in the free troposphere. The change in mixed-layer height, the depth over
which any input or loss at the surface or mixed-layer top is distributed, was shown to
be important for the budget of NO.

By comparing the lifetime of chemical active species with the boundary layer mix-
ing time through the dimensionless Damköhler number, we demonstrated an effective
method to obtain a first estimate of the relevance of dynamics and chemistry. When
classified into three regimes, the Damköhler number provides a measure of whether
chemistry is controlled by chemical transformations or ABL-dynamics. When calcu-
lated for a number of fast (OH), intermediate (\( \text{O}_3 \), \( \text{NO} \), \( \text{NO}_2 \)) and slow (CO) reacting
species, this method confirmed the impact of ABL-dynamics on the time evolution of
chemical active species.

Due to its simplicity and transparency, the mixed-layer model (MXLCH) used in this
study can act as a useful tool towards a better understanding of (1) the main chemical
pathways and processes that govern the temporal evolution of chemistry and (2) a
better understanding of the results obtained during measurement campaigns. Also,
gaining a better understanding of the core physical and chemical processes involved
might be beneficial for the development of new measurement campaigns or strategies,
or to understand new chemical pathways. MXLCH is available from the authors upon request.

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Ganzeveld, L., Eerdekens, G., Feig, G., Fischer, H., Harder, H., Königstedt, R., Kubistin, D.,


Sörgel, M., Regelin, E., Bozem, H., Diesch, J.-M., Drewnick, F., Fischer, H., Harder, H.,


Table 1. Chemical reaction scheme used in the reduced scheme with \( T \) the absolute temperature in Kelvin and \( \chi \) the solar zenith angle. First-order reaction rates are in \( s^{-1} \), second-order reaction rates in \( cm^3 \) molecule\(^{-1} \) \( s^{-1} \). In R19 \( n = 0 \) (no OH-recycling), \( P \) depicts a product which is not further evaluated in the chemical reaction scheme. ISO refers to isoprene, where all its oxidation products (MVK; methyl vinyl ketone and MACR; methacrolein) are lumped into a single species MVK.

<table>
<thead>
<tr>
<th>Number</th>
<th>Reaction</th>
<th>Reaction Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>( O_3 + hv \rightarrow O^1D + O_2 )</td>
<td>( 3.00 \times 10^{-5} \times e^{0.575 \frac{T}{298}} )</td>
</tr>
<tr>
<td>R2</td>
<td>( O^1D + H_2O \rightarrow 2OH )</td>
<td>( 1.63 \times 10^{-10} \times e^{60 \frac{T}{298}} )</td>
</tr>
<tr>
<td>R3</td>
<td>( O^1D + N_2 \rightarrow O_3 + P )</td>
<td>( 2.15 \times 10^{-11} \times e^{110 \frac{T}{298}} )</td>
</tr>
<tr>
<td>R4</td>
<td>( O^1D + O_2 \rightarrow O_3 )</td>
<td>( 3.30 \times 10^{-11} \times e^{50 \frac{T}{298}} )</td>
</tr>
<tr>
<td>R5</td>
<td>( NO_2 + hv \rightarrow NO + O_3 + P )</td>
<td>( 1.67 \times 10^{-2} \times e^{0.575 \frac{T}{298}} )</td>
</tr>
<tr>
<td>R6</td>
<td>( CH_2O + hv \rightarrow HO_2 + P )</td>
<td>( 1.47 \times 10^{-4} \times e^{0.575 \frac{T}{298}} )</td>
</tr>
<tr>
<td>R7</td>
<td>( OH + CO \rightarrow HO_2 + P )</td>
<td>( 2.40 \times 10^{-13} )</td>
</tr>
<tr>
<td>R8</td>
<td>( OH + CH_4 \rightarrow CH_2O_2 + P )</td>
<td>( 2.45 \times 10^{-12} \times e^{-1775} )</td>
</tr>
<tr>
<td>R9</td>
<td>( OH + ISO \rightarrow RO_2 )</td>
<td>( 1.00 \times 10^{-10} )</td>
</tr>
<tr>
<td>R10</td>
<td>( OH + MVK \rightarrow HO_2 + CH_2O + P )</td>
<td>( 2.40 \times 10^{-11} )</td>
</tr>
<tr>
<td>R11</td>
<td>( OH + HO_2 \rightarrow H_2O + O_2 )</td>
<td>( 4.80 \times 10^{-11} \times e^{250 \frac{T}{290}} )</td>
</tr>
<tr>
<td>R12</td>
<td>( OH + H_2O_2 \rightarrow H_2O + HO_2 )</td>
<td>( 2.90 \times 10^{-12} \times e^{-160 \frac{T}{298}} )</td>
</tr>
<tr>
<td>R13</td>
<td>( OH + O_3 \rightarrow HO_2 + O_2 )</td>
<td>( 1.30 \times 10^{-12} \times e^{950 \frac{T}{298}} )</td>
</tr>
<tr>
<td>R14</td>
<td>( HO_2 + NO \rightarrow OH + NO_2 )</td>
<td>( 3.50 \times 10^{-12} \times e^{250 \frac{T}{298}} )</td>
</tr>
<tr>
<td>R15</td>
<td>( CH_3O_2 + NO \rightarrow HO_2 + NO_2 + CH_2O + P )</td>
<td>( 2.80 \times 10^{-12} \times e^{300 \frac{T}{298}} )</td>
</tr>
<tr>
<td>R16</td>
<td>( RO_2 + NO \rightarrow HO_2 + NO_2 + MVK + CH_2O )</td>
<td>( 1.00 \times 10^{-11} )</td>
</tr>
<tr>
<td>R17</td>
<td>( OH + CH_2O \rightarrow HO_2 + P )</td>
<td>( 5.50 \times 10^{-12} \times e^{125 \frac{T}{298}} )</td>
</tr>
<tr>
<td>R18</td>
<td>( 2HO_2 \rightarrow H_2O_2 + O_2 )</td>
<td>( * )</td>
</tr>
<tr>
<td>R19</td>
<td>( CH_3O_2 + HO_2 \rightarrow P )</td>
<td>( 4.10 \times 10^{-13} \times e^{750 \frac{T}{298}} )</td>
</tr>
<tr>
<td>R20</td>
<td>( RO_2 + HO_2 \rightarrow nOH + P )</td>
<td>( 1.50 \times 10^{-11} )</td>
</tr>
<tr>
<td>R21</td>
<td>( OH + NO_2 \rightarrow HNO_3 )</td>
<td>( 3.50 \times 10^{-12} \times e^{840 \frac{T}{298}} )</td>
</tr>
<tr>
<td>R22</td>
<td>( NO + O_3 \rightarrow NO_2 + O_2 )</td>
<td>( 3.00 \times 10^{-12} \times e^{1500 \frac{T}{298}} )</td>
</tr>
<tr>
<td>R23</td>
<td>( NO_2 + O_3 \rightarrow NO_3 + O_2 )</td>
<td>( 1.40 \times 10^{-13} \times e^{2470 \frac{T}{298}} )</td>
</tr>
</tbody>
</table>

\( ^* k = (k_1 + k_2)/k_3; k_1 = 2.21 \times 10^{-13} \times e^{600 \frac{T}{298}}; k_2 = 1.91 \times 10^{-33} \times e^{980 \frac{T}{298}} \times c_{\text{air}}; k_3 = 1 + 1.4 \times 10^{-21} \times e^{2200 \frac{T}{298}} \times c_{H_2O} \)
Table 2. Initial and boundary conditions used in MXLCH. MXLCH is initiated at 07:00 UTC, $t$ is the elapsed time since the start of the simulation and $t_d$ is the time in seconds between 07:00–17:00 UTC.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial mixed-layer height</td>
<td>$h$ [m]</td>
</tr>
<tr>
<td></td>
<td>500</td>
</tr>
<tr>
<td>Horizontal velocity divergence</td>
<td>$\nabla \times \mathbf{V}_h$ [s$^{-1}$]</td>
</tr>
<tr>
<td></td>
<td>$5 \times 10^{-6}$</td>
</tr>
<tr>
<td>Geostrophic wind</td>
<td>$U_g, V_g$ [m s$^{-1}$]</td>
</tr>
<tr>
<td></td>
<td>(0.0)</td>
</tr>
<tr>
<td>Surface sensible heat flux</td>
<td>$\overline{w'\theta'_s}$ [K m s$^{-1}$]</td>
</tr>
<tr>
<td></td>
<td>$0.22 \sin(\pi t/t_d)$</td>
</tr>
<tr>
<td>Entrainment/surface heat-flux ratio</td>
<td>$\beta = \frac{-w'\theta'_h}{w'\theta'_s}$ [-]</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
</tr>
<tr>
<td>Initial mixed-layer potential temperature</td>
<td>$\langle \theta \rangle$ [K]</td>
</tr>
<tr>
<td></td>
<td>287</td>
</tr>
<tr>
<td>Initial free-troposphere potential temperature</td>
<td>$\theta_{FT}$ [K]</td>
</tr>
<tr>
<td></td>
<td>288.5</td>
</tr>
<tr>
<td>Potential temperature lapse rate free troposphere</td>
<td>$\gamma_\theta$ [K m$^{-1}$]</td>
</tr>
<tr>
<td></td>
<td>0.006</td>
</tr>
<tr>
<td>Surface latent heat flux</td>
<td>$\overline{w'q'_s}$ [kg kg$^{-1}$ m s$^{-1}$]</td>
</tr>
<tr>
<td></td>
<td>$0.03 \sin(\pi t/t_d)$</td>
</tr>
<tr>
<td>Initial mixed-layer specific humidity</td>
<td>$\langle q \rangle$ [g kg$^{-1}$]</td>
</tr>
<tr>
<td></td>
<td>5.3</td>
</tr>
<tr>
<td>Initial free-troposphere specific humidity</td>
<td>$q_{FT}$ [g kg$^{-1}$]</td>
</tr>
<tr>
<td></td>
<td>4.5</td>
</tr>
<tr>
<td>Specific humidity lapse rate free troposphere</td>
<td>$\gamma_\theta$ [g kg$^{-1}$ m$^{-1}$]</td>
</tr>
<tr>
<td></td>
<td>$-0.0012$</td>
</tr>
</tbody>
</table>
Table 3. Overview experiments

<table>
<thead>
<tr>
<th>Name</th>
<th>Dynamics</th>
<th>Chemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>BOX750</td>
<td>NONE</td>
<td>Reduced</td>
</tr>
<tr>
<td>MOZART</td>
<td>MXLCH</td>
<td>MOZART</td>
</tr>
<tr>
<td>REDUCED</td>
<td>MXLCH</td>
<td>Reduced</td>
</tr>
</tbody>
</table>
Table 4. Initial mixing ratio in both MOZART and the reduced scheme in the mixed-layer (⟨S⟩) and free troposphere (SFT), and surface emission or deposition. All other species except for molecular oxygen and nitrogen are initialized at zero. The chemistry scheme is initialised at 07:00 UTC, t is the elapsed time since the start of the simulation and td is the time in seconds between 07:00–17:00 UTC.

<table>
<thead>
<tr>
<th></th>
<th>O3 [ppb]</th>
<th>NO</th>
<th>NO2</th>
<th>CH4</th>
<th>ISO</th>
<th>CO</th>
<th>H2O2</th>
</tr>
</thead>
<tbody>
<tr>
<td>⟨S⟩</td>
<td>31</td>
<td>0</td>
<td>0.6</td>
<td>1724</td>
<td>0</td>
<td>105</td>
<td>0.1</td>
</tr>
<tr>
<td>SFT [ppb]</td>
<td>39</td>
<td>0</td>
<td>0</td>
<td>1724</td>
<td>0</td>
<td>105</td>
<td>0.1</td>
</tr>
<tr>
<td>w′S′ [µg m⁻² s⁻¹]</td>
<td>0</td>
<td>0.04</td>
<td>*</td>
<td>0</td>
<td>**</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

* Deposition flux of NO2 is calculated as \(-v_C C_{NO2}\) with \(v_C = 0.015 \text{ m s}^{-1}\)

**\(w′ISO′ = 0.09 \cdot \sin(\pi t/td)\)**
Fig. 1. Conceptual representation of the vertical profiles of specific humidity \( (q) \), potential temperature \( (\theta) \) and, as an example, nitrogen dioxide \( (\text{NO}_2) \) and ozone \( (\text{O}_3) \). Within the mixed-layer all variables are constant with height (Eq. 1), topped by an inversion defined as \( \Delta \phi = \phi_{\text{FT}} - \langle \phi \rangle \) (Eq. 3). On the right side the for chemistry relevant processes are shown with emissions and deposition near the surface, chemical reactions within the mixed-layer and entrainment of free-tropospheric air at the mixed-layer top \( \langle \phi' \rangle_h \), Eq. 2).
Fig. 2. Forward trajectories at 100 m and 2000 m calculated by the NOAA HYSPLIT model using NCEP-GDAS meteorology, starting at Sevilla and Huelva at 08:00 UTC (solid lines) and 12:00 UTC (dashed lines) on 23 November 2008. The black dot indicates the DOMINO measurement location at El Arenosillo.
Fig. 3. Time evolution of the (a) mixed-layer height, (b) slab averaged potential temperature, (c) slab averaged specific humidity and (d) photolysis rate of NO$_2$, compared to the measurements. In addition to the results of MXLCH, the fixed conditions of the box model are indicated.
Fig. 4. Measured and modelled mixed-layer mixing ratios of $\text{O}_3$, NO, $\text{NO}_2$ and $\text{HNO}_3$ as measured and modelled with MXLCH (using both MOZART and the reduced chemical scheme) and the box model (using the reduced chemistry scheme).
Fig. 5. Measured and modelled mixed-layer mixing ratios of Isoprene, OH, HO₂ and H₂O₂ as measured and modelled with MXLCH (using both MOZART and the reduced chemical scheme) and the box model (using the reduced chemistry scheme).
Fig. 6. Individual budget terms of Eq. (8) for O$_3$, NO, NO$_2$ and OH. The labels of the individual terms refer to the notation defined in Eq. (8).
Fig. 7. Calculated life times of key chemical species and the ABL (top) and the OH-reactivity (bottom), the inverse of the OH lifetime, as measured and modelled.