The vertical structure of OH-HO\textsubscript{2}-RO\textsubscript{2} chemistry in the nocturnal boundary layer: A one-dimensional model study

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[1] Elevated OH and peroxy radical levels have recently been observed in the nocturnal boundary layer (NBL). Despite the possible importance of OH for the gas phase and particulate composition, the source of these RO\textsubscript{x} radicals at night is currently unclear. To investigate the influence of vertical mixing on nocturnal RO\textsubscript{x} chemistry, calculations with a one-dimensional chemical transport model were performed. The model predicts distinct vertical profiles for all RO\textsubscript{x} radical species during the night, with a pronounced RO\textsubscript{2} maximum aloft and maxima of HO\textsubscript{2} and OH closer to the ground. We conceptualize our results by distinguishing three chemical regimes in the NBL: (1) In the unreactive ground layer, which only forms at high NO emissions and strong vertical stabilities, OH chemistry is suppressed by high NO levels. (2) The upper layer, located in the upper NBL, is decoupled from the NO emissions at the ground. Ozonolysis of volatile organic compounds (VOCs) leads to the formation of \(\sim 10^5\) molecules cm\(^{-3}\) of OH. The RO\textsubscript{2} maximum develops in the lower part of the upper layer by the elevated O\textsubscript{3}/NO\textsubscript{3} + VOC reaction rates. (3) In the reactive mixing layer, in the height interval between the upper layer and the ground layer, RO\textsubscript{2} and HNO\textsubscript{4} (as HO\textsubscript{2} reservoir) from the upper layer are mixed with NO from the ground layer. The active radical propagation chain leads to distinctive maxima of HO\textsubscript{2} and OH (up to several \(10^6\) molecules cm\(^{-3}\)) in this layer. The OH radicals in the reactive mixing layer can contribute up to 43% to the nocturnal VOC oxidation, illustrating that OH chemistry can be important even at night. Our model simulations show that vertical transport can redistribute RO\textsubscript{x} radicals in the NBL, acting as an important radical source in the lowest few meters of the atmosphere. INDEX TERMS: 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; KEYWORDS: nocturnal chemistry, radical chemistry, chemical transport modeling


1. Introduction

[2] For many years it was accepted that elevated levels of OH and peroxy radicals are present only in the daytime atmosphere. However, recent field experiments have found elevated levels of RO\textsubscript{x} radicals (the term RO\textsubscript{x} comprises organic peroxy radicals, RO\textsubscript{2}, HO\textsubscript{2}, and OH) at night in both urban and rural areas [Mihelcic et al., 1993; Hu and Stehman, 1995; Tanner and Eisele, 1995; Cantrell et al., 1996a, 1996b, 1997; Monks et al., 1996; Carslaw et al., 1997; George et al., 1999; Kanaya et al., 1999; Falloona et al., 2001; Geyer et al., 2003; Holland et al., 2003; Mihelcic et al., 2003; Ren et al., 2003]. Nocturnal OH concentrations exceeding \(2 \times 10^6\) molecules cm\(^{-3}\) have been observed. It is now believed that OH radicals are formed during the night by two major mechanisms: a reaction chain initiated by reactions of NO\textsubscript{3} with volatile organic compounds (VOCs) and the ozonolysis of alkenes [Daele et al., 1995; Paulson et al., 1999; Paulson and Orlando, 1996; Platt et al., 1990].

[3] RO\textsubscript{2}, produced by the NO\textsubscript{3} + VOC reactions, acts as a precursor to OH through its subsequent oxidation to HO\textsubscript{2} and OH by reactions with NO (and, to a minor extent, NO\textsubscript{3} and RO\textsubscript{2}):

\[
\text{VOC} \xrightarrow{\text{NO}_3} \text{RO}_2 \xrightarrow{\text{NO(RO}_2)} \text{HO}_2 \xrightarrow{\text{NO(RO}_2)} \text{OH}
\]

Positive correlations between [RO\textsubscript{2}] and [NO\textsubscript{3}] suggest that NO\textsubscript{3} + VOC reactions are the main source for peroxy...
radicals at night [Connell et al., 1997; Geyer et al., 2003; Mihelcic et al., 1993]. In the presence of 40 parts per trillion (ppt) of RO$_2$, as observed by Mihelcic et al. [1993], reaction chain (1) could indeed lead to a significant formation of OH. Efficient generation of OH through reaction (1) can occur in the simultaneous presence of NO$_3$, as a VOC oxidant, and NO$_2$ as a fast chain carrier, converting RO$_2$ into OH [Geyer et al., 2003]. However, the presence of NO$_3$ and NO in one air mass is unlikely from a purely chemical standpoint, since the two molecules undergo a very fast reaction, forming 2 NO$_2$ molecules [Geyer et al., 2003]. It is thus often assumed that reaction chain (1) propagates through the much slower RO$_2$ + NO$_3$ and RO$_2$ + RO$_2$ reactions, and it is therefore less efficient as an OH source. Ozonolysis of unsaturated hydrocarbons is another production path for OH and peroxy radicals at night [Paulson et al., 1997, 1999; Donahue et al., 1998; Neeb and Moortgat, 1999]. Paulson and Orlando [1996] state that this mechanism can be the dominant OH source at night in forested and suburban areas. In contrast to propagation chain (1), NO is not necessary for the efficient production of OH in this case.

[4] In recent years, nocturnal OH chemistry has been investigated in several box model studies [Bey et al., 1997, 2001; Harrison et al., 1998; Götz et al., 2001; Geyer et al., 2003]. Most of these studies found that the majority of OH is directly formed by ozonolysis of VOCs. However, these box model calculations were unable to explain the high OH levels observed in several field experiments. The results also showed that reaction chain (1) proceeded slowly, since high NO levels lead to low NO$_3$ concentrations in the box models.

[5] Studies of nocturnal OH chemistry have thus far relied on a zero-dimensional approach, by either measuring the radicals at a single altitude or applying box models for the interpretation of the data. However, stable vertical stratification in the nocturnal boundary layer (NBL) and weak vertical mixing, combined with direct emissions of NO and VOCs near the ground, can lead to an altitude-dependent chemistry and to pronounced gradients of many trace gases [Geyer and Stutz, 2004; Stutz et al., 2004]. The vertical transport caused by the trace gas gradients can have a strong influence on the concentrations of radical precursors and free radicals, including NO, O$_3$, NO$_3$, and N$_2$O$_5$ [Geyer and Stutz, 2004]. A zero-dimensional view of nocturnal chemistry that neglects vertical transport processes may therefore not be appropriate.

[6] In this paper we investigate the influence of vertical mixing on the development of vertical profiles of RO$_2$, HO$_2$, and OH and the altitude dependence of OH chemistry in the nocturnal boundary layer by means of a highly resolved one-dimensional chemistry transport model. The radical formation processes in various parts of the NBL will be discussed, and chemical transport mechanisms that lead to the formation of radicals at certain altitudes will be presented. To assess the importance of nocturnal OH, the oxidation of VOCs and NO$_2$ will be studied.

2. Model Description

[7] This study was performed using an expanded version of the vertically highly resolved one-dimensional (1-D) Nocturnal Chemistry and Transport model (NCAT) [Geyer and Stutz, 2004], which includes the Regional Atmospheric Chemistry Mechanism (RACM) [Stockwell et al., 1997]. NCAT is based on a system of 1-D transport kinetics equations, which express the change of the concentration $c(z, t)$ of a trace gas $i$ at an altitude $z$ at the time $t$ as

$$\frac{dc(z, t)}{dt} = \Psi_i(z, t) + P_i(z, t) - L_i(z, t) + \xi_i(z, t). \quad (2)$$

[8] Here $\Psi_i(z, t) = -[\partial j_i(z, t)/\partial z]$ is the rate of the concentration change caused by a vertical flux $j_i(z, t)$, $P_i(z, t)$ is the total chemical production rate, $L_i(z, t)$ is the total chemical loss rate, and $\xi_i(z, t)$ is the emission rate of a compound $i$. This equation system is solved with a Gear-type solver [Curtis and Sweetenham, 1987]. In this study, the model subdivides the lowest 250 m of the nocturnal atmosphere into 20 boxes. Box heights increase logarithmically below 1 m and linearly above 1 m. The variations of trace gas concentrations are calculated for 6 hours following model start. Because the intention of this study is to investigate general features of vertically resolved nocturnal OH-HO$_2$-RO$_2$ chemistry, rather than to realistically simulate the evolution of vertical profiles in the atmosphere during the night, the emission rates and meteorological parameters are kept constant throughout the model run.

[9] Vertical fluxes are calculated by a first-order flux-gradient relationship (K model). As discussed by several authors [Brost et al., 1988; Fitzjarrald and Lenschow, 1983; Galmarini et al., 1997; Geyer and Stutz, 2004; Hamba, 1993; Vilà-Guerau de Arellano et al., 1995], chemistry can alter the vertical flux of a species if (1) the concentration of the species is far from the pseudo chemical steady state concentration and (2) the chemical timescale of a reaction of the species is on the order of the turbulence timescale. Under these conditions the net vertical flux of a compound can be calculated by a modified K model [Geyer and Stutz, 2004]. In our previous study of the NBL we found that it is sufficient to apply the modified K model for NO [Geyer and Stutz, 2004]. The effect of chemistry on the vertical fluxes of all other compounds was found to be small, and therefore the original K model (see $K_{\text{inert}}$ of equation (3)) was used. The modified K model was applied to the calculation of the vertical flux of NO by using the following set of equations: Using the definition

$$K_{\text{inert}}(z, t) = \frac{k_{\text{av}}(i)z}{\Phi_s(z, t)}, \quad (3)$$

the flux of NO is expressed by

$$j_{\text{NO}}(z, t) = -K_{\text{inert}}(z, t) \left\{ \frac{\partial c_{\text{NO}}(z, t)}{\partial z} + \frac{\partial}{} \frac{\partial c_{\text{NO}}(z, t)}{\partial z} - \frac{\partial c_{\text{NO}}(z, t)}{\partial z} \right\}_{\text{NO eff}(z, t)}. \quad (4)$$
mechanism. In addition to the reactions in RACM we also consider the direct formation of peroxy and OH radicals by ozonolysis of VOCs, forming a wide variety of secondary VOCs (mostly aromatics, and nine carbonyls). RACM distinguishes 24 different types of organic peroxy radicals, which are formed by the oxidation of VOCs initiated by NO3, O3, and OH. The RO2 radicals can react with NO, NO3, and other RO2 radicals, forming a wide variety of secondary VOCs (mostly carbonyls) as well as HO2. The hydroperoxy radical is further converted into OH, for example, by reactions with NO. It is important to note that in the case of the OH + VOC reactions, one peroxy radical is formed in RACM; that is, these reactions are neutral in [OH] [Stockwell et al., 1997]. The direct formation of peroxy and OH radicals by ozonolysis [Paulson and Orlando, 1996] is also part of the RACM mechanism. In addition to the reactions in RACM we included the gas phase reaction of N2O5 with water vapor (first and second order in H2O) in the NCAT model [Wahner et al., 1998].

In equation (5), $k_{\text{NO,Lim}}$ represents the rate constant of a bimolecular reaction with NO. The turbulence timescale $\tau_{\text{turbulent}}(z, t)$ is on the order of 100 s in the NBL [Fitzjarrald and Lenschow, 1983; Lenschow, 1981].

$\tau_{\text{eff}}(z, t) = \frac{1}{\tau_{\text{turbulent}}(z, t) + \sum_{i,m} k_{\text{NO,Lim}}(c_i + c_m)}$ (5)

Table 1. Variable Parameters of the Model Scenarios

<table>
<thead>
<tr>
<th>Characterization</th>
<th>$K$ at 10 m, m$^2$s$^{-1}$</th>
<th>$T$ at 10 m, K</th>
<th>Emission Rate of NO From Cars at 0.1–1 m, molecules cm$^{-2}$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urban base run and sensitivity studies</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>1 weak stability/moderate emissions</td>
<td>0.30</td>
<td>290</td>
<td>$4 \times 10^9$</td>
</tr>
<tr>
<td>2 weak stability/low emissions</td>
<td>0.30</td>
<td>290</td>
<td>$1 \times 10^9$</td>
</tr>
<tr>
<td>3 weak stability/high emissions</td>
<td>0.30</td>
<td>290</td>
<td>$12 \times 10^9$</td>
</tr>
<tr>
<td>4 weak stability/very high emissions</td>
<td>0.30</td>
<td>290</td>
<td>$30 \times 10^9$</td>
</tr>
<tr>
<td>5 strong stability/moderate emissions</td>
<td>0.06</td>
<td>290</td>
<td>$4 \times 10^9$</td>
</tr>
<tr>
<td>6 neutral conditions/moderate emissions</td>
<td>1.00</td>
<td>290</td>
<td>$4 \times 10^9$</td>
</tr>
<tr>
<td>7 scenario 1 at low temperatures</td>
<td>0.30</td>
<td>275</td>
<td>$4 \times 10^9$</td>
</tr>
<tr>
<td>8 scenario 1 at high temperatures</td>
<td>0.30</td>
<td>305</td>
<td>$4 \times 10^9$</td>
</tr>
<tr>
<td>Rural case</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9 strong stability/high emissions</td>
<td>0.06</td>
<td>290</td>
<td>$12 \times 10^9$</td>
</tr>
<tr>
<td>10 weak stability/moderate emissions</td>
<td>0.30</td>
<td>290</td>
<td>$10 \times 10^6$</td>
</tr>
</tbody>
</table>

[10] The effective time $\tau_{\text{eff}}$ was approximated according to Hamba [1987], who used the two-scale direct interaction approximation theory [Yoshizawa, 1982]:

$\tau_{\text{NO eff}}(z, t) = \frac{1}{\tau_{\text{turbulent}}(z, t) + \sum_{i,m} k_{\text{NO,Lim}}(c_i + c_m)}$ (5)

[11] NO is emitted from the soil (at 10$^{10}$ molecules cm$^{-2}$ in all scenarios) as well as from traffic between 0.1 and 1 m in urban scenarios (Table 1). The traffic NO emission rate of 4 $\times 10^9$ molecules cm$^{-3}$ in the base run is varied from 1 $\times 10^9$ to 30 $\times 10^9$ molecules cm$^{-3}$ in scenarios 2–4. Using the emission ratios measured by Kurtenbach et al. [2001, 2002], anthropogenic emissions of VOCs (alkanes)/[NO] = 0.18, (alkenes)/[NO] = 0.44, (aromatics)/[NO] = 0.13, (carbons)/[NO] = 0.06, CO ([CO]/[NO] = 6), NO2 ([NO2]/[NO] = 0.058), and HONO ([HONO]/[NO] = 0.008) are also considered. Biogenic emissions of monoterpenes (RACM classes API: α-pinene and other cyclic terpenes with one double bond and LIM: d-limonene and other cyclic diene-terpenes), at an emission ratio of API/LIM = 2, are included in the model between 1 and 10 m altitude. The API emission rate at 290 K was set to 3 $\times 10^6$ molecules cm$^{-3}$ in the urban scenarios. In the rural scenario a representative value of 10 $\times 10^6$ molecules cm$^{-3}$ was chosen (Table 1). Emissions of isoprene are negligible at night [Guenther et al., 1996] and were thus not included in the model runs. Note that the monoterpen emission rate exponentially increases with temperature [Guenther et al., 1993].

[14] The temperature $T$ at 10 m altitude is set to 290 K in most cases, with the exception of scenario 7 (275 K) and scenario 8 (305 K). The eddy diffusivity $K$ at 10 m altitude varied from 0.06 m$^2$s$^{-1}$ in scenario 5 to 1 m$^2$s$^{-1}$ in scenario 6. In all other cases, $K$ is set to 0.3 m$^2$s$^{-1}$ (Table 1). The gradients of $K$ are calculated from micrometeorological parameters (equation (3)). The temperature gradients were calculated according to $dH(z, t)/dz = -[H(z, t)/\rho c_p](1/\kappa u^* r(t) - \Phi_d z/L^2, t)$ [Araya, 1988; Haugen, 1973]. Here $\rho c_p$ represents the mass heat capacity of air, $\rho$ represents its density, and $\Phi_d z/L^2, t$ is the dimensionless correction factor for heat transport suggested by Businger et al. [1971]. In the very stable case of scenario 5 the temperature gradient is $-0.08$ K m$^{-1}$ over the lowest 100 m, while the gradient is $-0.01$ K m$^{-1}$ in the neutrally stable scenario 6. In all other cases a slightly positive temperature gradient of $+0.01$ K m$^{-1}$ in the lowest 100 m is found.
Vertical Structure of Nocturnal OH-HO2-RO2 Chemistry

To provide a detailed analysis of the vertical variation of OH chemistry and its precursors, RO2 and HO2, we have chosen an urban scenario with moderate NO emission and weak temperature inversion (scenario 1 in Table 1) as a base case. The model results for this scenario will be discussed in detail in sections 3.1–3.2. In section 3.3 we introduce a description of NBL chemistry based on three vertical layers with distinct characteristics. This three-layer model simplifies the discussion of the sensitivity studies in section 3.5. Equations for the pseudo steady state concentrations of peroxy radicals and OH are derived in section 3.4. Finally, we discuss nocturnal chemistry in a highly polluted urban and a rural environment in sections 3.6 and 3.7. In sections 3.1–3.7 we focus on the lowest 100 m of the NBL.

3.1. Vertical Profiles in a Weakly Stable Urban Case

In scenario 1 the shapes of the RO2 profiles do not change during the night. However, the overall levels of RO2, HO2, and OH decrease. After 1 hour a mixing ratio of 90 ppt is predicted for the RO2 maximum. Close to the ground, RO2 decreases to 10 ppt. At 100 m altitude the RO2 mixing ratio reaches 70 ppt. After 2 hours, when isoprene and other substances produced during the previous day have been destroyed and the high mixing ratio of O3 has decreased, the RO2 levels drop by roughly 20 ppt. In the following 4 hours the RO2 concentration slowly continues to decrease. In scenario 1, NO3-alkene adducts and peroxy radicals formed from the oxidation of ethane and toluene are the most abundant RO2 species. At the altitude of the HO2 maximum, HO2 levels are as high as 5.4 ppt after the first hour. They decrease to <3 ppt directly above the ground. At 100 m, [HO2] is ~2 ppt. After 6 hours the HO2 mixing ratio decreases to 4.5 ppt. While after 1 hour OH levels are 5 × 10^6 molecules cm^-3 above 20 m, [OH] reaches a maximum concentration of 1.8 × 10^6 molecules cm^-3 in the lowest meter of the NBL. After 6 hours the OH maximum has decreased to <1.4 × 10^6 molecules cm^-3.

The interpretation of the vertical profiles of the peroxy radicals and OH requires the analysis of the vertical distribution of their individual production and loss paths. These rates depend on the vertical concentration profiles of NO, O3, NO2, NOx, and VOCs. Figure 2 shows hourly snapshots of the vertical profiles of [NO], [O3], [NO2], [NOx], and the two RACM VOC classes, OLI (internal alkene) and API (α-pinene and other cyclic terpenes with one double bond).

After 1 hour, NO reveals a strong negative gradient, with levels of 2.5 ppb in the lowest meter and <1 ppt above 10 m. The extent of the layer with high [NO] slowly grows throughout the night, and the level of NO at the ground increases. The NO profile is caused by its fast reaction with O3 during the upward transport from its emission height. O3 shows a weak positive gradient. After 1 hour the
initially uniform \(O_3\) mixing ratio of 100 ppb is reduced to 96 ppb at 100 m altitude, while <80 ppb remain directly above the ground. \(O_3\) levels are reduced by 20–30 ppb after 6 hours. The ozone loss is predominantly caused by titration with NO. Deposition and reactions with VOCs play a minor role. Because of the fast reaction rate of NO and \(O_3\) near the ground, NO2 develops a negative gradient in the NBL. After 1 hour the mixing ratio of NO2 is 28 ppb in the lowest meter, while the initial 10 ppb are still present at 100 m altitude. During the night the NO2 levels slowly increase. The model also predicts a strong positive gradient of \([NO_3]\), with 1 hour NO3 mixing ratios decreasing from 18 ppt above 50 m to <2 ppt in the lowest meter. After 6 hours NO3 levels are reduced by ~25%. The NO3 profile is caused by the reaction of NO3 with NO in the lower part of the NBL.

In summary, the slow upward transport of NO emitted near the ground and the simultaneously occurring chemistry, in particular, the reactions of NO with \(O_3\) and NO3, control the vertical structure of the chemistry of NOx, \(NO_3\), and VOCs. In the case of \(NO_2\) and \(O_3\), dry deposition is also significant. Vertical transport of \(N_2O_5\) can play an important role and is often the main source of NO3 radicals near the ground [Geyer and Stutz, 2004]. The two parameters controlling the shape of the various profiles are the NO emission rate and the vertical stability. In general, higher emissions and stronger stabilities will lead to stronger gradients. For a more detailed discussion of the development of the vertical profiles of nitrogen oxides and \(O_3\), refer to Geyer and Stutz [2004].

The different VOC classes included in RACM develop specific vertical profiles in the NBL depending on their lifetime and the dominant oxidant and its vertical profile. All VOCs show a negative concentration gradient because they are emitted or are predominantly chemically formed in the lowest 10 m. Alkanes and aromatics, which have a long lifetime and can be well mixed, show only a very weak negative gradient during the night. Similarly, carbonyls develop a very weak negative gradient. The concentrations of these long-lived species slowly increase during the night because their emission rate is higher than their oxidation rate. Alkenes and monoterpenes have a relatively short lifetime because of their reactions with NO3 and \(O_3\). Consequently, this group develops strong negative gradients and can reach steady state during the night. Figure 2 shows the vertical profiles of the RACM VOC classes OLI and API as examples for these VOC groups. While \([O_3]\) is as high as 1 ppb in the lowest meter, its concentration is negligible above ~80 m. Similarly, \([API]\) is ~50 ppt at its emission heights (1–10 m) but does not reach altitudes above 70 m. Other compounds, such as \(CO\), \(H_2O_2\), and HNO3, develop weak negative gradients because they are either emitted (CO) or are chemically produced near the ground and only slowly transported upward. \(CO\) in the lowest meter increases from 300 to 500 ppb in the first 6 hours of the night. Similarly, \([H_2O_2]\) levels grow from 20 to 50 ppt, and \([HNO_3]\) increases from 0.5 to 3 ppt near the ground. HNO3 develops a vertical profile similar to that of \(HO_2\). Its mixing ratio is as high as 130 ppt a few meters above the ground.

3.2. Altitude Dependence of \(RO_x\) Chemistry in the NBL

In this section we investigate the origin of the nocturnal \(RO_x\) profiles shown in Figure 1 for the weakly stable urban case. In particular, the cause of the pronounced concentration maxima at specific altitudes is discussed.

Figure 3 shows the vertical profiles of the various formation, destruction, and vertical transport rates of \(RO_2\), \(HO_2\), and \(OH\) in scenario 1, 3 hours after model start. The nomenclature of the rates follows that used in equation (2): \(P_{A=B+C}\) is a production rate of compound \(A\) due to the reaction \(B + C\), \(L_{A=D}\) is a loss rate of compound \(A\) due to reaction with \(D\), and \(\Psi_A\) is the rate of concentration change of compound \(A\) due to vertical transport.

3.2.1. \(RO_2\) Radicals

The main chemical source for \(RO_2\) radicals during the early night is the reaction of unsaturated VOCs with NO3 followed by \(O_2\) addition, forming nitratealkylperoxy radicals. The reaction of NO3 with internal alkenes dominates in scenario 1 (60%), followed by the reaction with monoterpenes (20%). Terminal alkenes and dienes contribute another 15%. The product of the positive NO3 and negative VOC gradients (Figures 2d–2f) causes a broad maximum of \(P_{RO_2=NO_3+VOCs}\) of \(\sim 10^7\) molecules cm\(^{-3}\) s\(^{-1}\) in the lowest 30 m. The production rate slowly decreases with altitude to \(\sim 2 \times 10^6\) molecules cm\(^{-3}\) s\(^{-1}\) at 100 m and \(\sim 5 \times 10^5\) molecules cm\(^{-3}\) s\(^{-1}\) at the ground. Ozonolysis of alkenes (with a contribution of internal alkenes of 75%) is another important source for peroxy radicals in the NBL. \(P_{RO_2=O_3+VOCs}\) shows...
Figure 3. Vertical profiles of chemical rates and the rate of change by vertical transport of RO₂, HO₂, and OH 3 hours after model start for scenario 1. See color version of this figure at back of this issue.

a weak negative gradient and peaks at $5 \times 10^6$ molecules cm$^{-3}$ s$^{-1}$ at the ground. At 100 m, $P_{RO₂-O₃+VOC}$ has decreased to $6 \times 10^5$ molecules cm$^{-3}$ s$^{-1}$. Organic peroxy radicals are also formed by reactions of OH radicals with VOCs. $P_{RO₂-OH+VOC}$ strongly increases toward the ground, peaking at $3.6 \times 10^7$ molecules cm$^{-3}$ s$^{-1}$ in the lowest meter. However, because one OH radical is also destroyed in RACM by this reaction, $P_{RO₂-OH+VOC}$ is ultimately not a net source of RO₂ radicals in the NBL.

[26] Two major loss paths for RO₂ are active in the NBL: reaction with NO and reactions with other RO₂ radicals. Reaction with NO, which is negligible above 15 m because of low [NO], is the dominating RO₂ loss path in the lowest 10 m, peaking at $4.5 \times 10^7$ molecules cm$^{-3}$ s$^{-1}$ at the ground. $L_{RO₂-NO}$ has a strong negative gradient caused by the negative gradient of [NO] (Figure 2f). $L_{RO₂-RO₂}$ has a maximum of $6 \times 10^6$ molecules cm$^{-3}$ s$^{-1}$ at ~15 m. The $L_{RO₂-RO₂}$ profile is similar to the vertical profile of RO₂. RO₂ radicals can also be destroyed by reaction with NO₃ and, in the case of alkyl radicals, by reaction with NO₂ forming PANs. Note that $L_{RO₂-NO2PAN}$ in Figure 3a is corrected for the thermal decay of PANs back to RO₂ and NO₂. In scenario 1, $L_{RO₂-NO}$ and $L_{RO₂-NO2PAN}$ are less important.

[27] The RO₂ maximum at ~20 m shown in Figure 1a is caused by the broad peak of $P_{RO₂-NO3+VOC}$ in the lowest 30 m and the strong negative gradient of $L_{RO₂-NO}$. From this maximum, RO₂ is transported downward and, to a minor extent, upward. Considering that $Ψ_{RO₂}$ is proportional to the gradient of the vertical RO₂ flux (see section 2), vertical mixing acts as a sink of RO₂ between 7 and 30 m and as a source of RO₂ in the lowest 7 m. Vertical transport strongly influences the RO₂ concentration in the lower part of the NBL (Figure 3a). At 10 m, for example, the contribution of vertical transport to the total RO₂ loss is ~25%. In the lowest meter, $Ψ_{RO₂}$ is the main net source for organic peroxy radicals.

3.2.2. HO₂ Radicals

[28] The reaction of RO₂ radicals with NO is by far the most important HO₂ source in the lowest NBL. Similar to $L_{RO₂-NO}$, $P_{HO₂-RO₂}$ increases toward the ground, peaking at almost $4 \times 10^4$ molecules cm$^{-3}$ s$^{-1}$. Other important HO₂ production paths include the conversion of OH into HO₂ by reaction with CO and the ozonolysis of alkenes. $P_{HO₂-OH+CO}$ is highest close to the ground, where it reaches $10^7$ molecules cm$^{-3}$ s$^{-1}$. $P_{HO₂-RO₂}$ has a negative gradient in the lower NBL, with a maximum of $2 \times 10^6$ molecules cm$^{-3}$ s$^{-1}$ close to the ground. Other HO₂ sources, for example, the conversion of RO₂ into HO₂ by reaction with NO₃ and other RO₂ radicals or direct formation by NO₃ + VOC reactions, are unimportant in scenario 1.

[29] The dominant sink of HO₂ in the lowest ~5 m is its reaction with NO₃ forming OH radicals, $L_{HO₂-NO₃}$. This loss path is dominant above 6 m, with a broad maximum at 15 m ($3 \times 10^5$ molecules cm$^{-3}$ s$^{-1}$). Other loss paths of HO₂ such as uptake on aerosols or the reactions with NO₃ and O₃ are unimportant in scenario 1.

[30] While RO₂ can be vertically transported, the lifetime of HO₂ is too short to allow significant transport rates ($Ψ_{HO₂}$ in Figure 3b). However, HO₂ can be transported indirectly via transport of its reservoir species HNO₄, which is formed by reaction of HO₂ radicals with NO₂ (lifetime ~30 s at 290 K). We define the net production rate of HO₂ from HNO₄ decay as

$$P_{HO₂-HNO₄} = f_{HNO₄}[HNO₄] - k_{HO₂-NO₂}[HO₂][NO₂].$$
In equation (6), and in the remainder of the paper, \( f_X \) and \( k_{Y+Z} \) represent the unimolecular rate constant for thermal dissociation of a gas \( X \) and the rate constant of the reaction \( Y + Z \), respectively. As shown in Figure 3b, \( P_{\text{HO2}+\text{HNO4}} \) is negative between 2 and 12 m (down to \( -9 \times 10^9 \) molecules cm\(^{-3} \) s\(^{-1} \)), while it is positive in the lowest 2 m and between 12 and 40 m. The positive \( P_{\text{HO2}+\text{HNO4}} \) near the ground is caused by the high HO2 loss rate \( L_{\text{HO2}+\text{NO}} \), which leads to low HO2 mixing ratios at this height. Consequently, less HNO4 can be produced by the HO2 + NO reaction near the ground, and HNO4 develops a positive gradient. Therefore HNO4 is transported toward the ground, where its thermal decay acts as a net HO2 source. As shown in section 3.6, \( P_{\text{HO2}+\text{HNO4}} \) is an important source of HOx radicals near the ground during strong vertical stabilities and high traffic emissions.

3.2.3. OH Radicals

Only two paths are efficient in the formation of OH radicals in the nighttime atmosphere: reaction of HO2 with NO and ozonolysis of unsaturated VOCs. Other OH sources, such as the reaction of HO2 with NO\(_3\), are negligible in scenario 1. \( P_{\text{OH}+\text{HO2}+\text{NO}} \) increases toward the ground because of the strong negative gradient of [NO]. The rate exceeds \( P_{\text{OH}+\text{O3}+\text{VOCs}} \) below \( \sim 7 \) m and reaches a maximum level of \( 5.2 \times 10^7 \) molecules cm\(^{-3} \) s\(^{-1} \) in the lowest meter. At higher altitudes, OH is predominantly formed by the ozonolysis of alkenes. \( P_{\text{OH}+\text{O3}+\text{VOCs}} \) shows a weak negative gradient and decreases to \( 5 \times 10^5 \) molecules cm\(^{-3} \) s\(^{-1} \) at 100 m altitude.

Because of the negative vertical profile of [OH], all its loss rates show a negative gradient, although the individual loss frequencies are only weakly altitude-dependent. In scenario 1 the highest OH loss rates result from the reaction of OH with VOCs, NO\(_2\), and CO. The strong peak of \( P_{\text{OH}+\text{HO2}+\text{NO}} \) close to the ground and the weak altitude dependence of the OH sinks cause the maximum of the OH concentration shown in Figure 1c. Vertical transport of OH is unimportant (\( P_{\text{OH}} \) in Figure 3c).

3.3. Layer Concept of the NBL

To conceptualize the vertical change in the OH-HO2-RO2 chemistry at night, we introduce a three-layer view of the NBL. We distinguish three chemical regimes that occupy different height intervals in the NBL on the basis of the mechanism and efficiency of the OH production. OH is produced at night by the ozonolysis of alkenes and by reactions of peroxy radicals with NO (section 3.2.3). For the latter mechanism (equation (1)) to be efficient, O3 or NO3 radicals must be present to produce RO2 radicals by the oxidation of VOCs, and NO concentrations must be high enough to convert these peroxy radicals into HO2 and OH. We have therefore chosen the reaction rate of NO with O3 as an indicator for the vertical extent of these layers. This rate is easy to determine, both experimentally in the atmosphere and in models. Note that the nitrate radical is linked to O3 by its production from the O3 + NO2 reaction.

Figure 4 shows the vertical profile of the O3 + NO reaction rate 1, 3, and 6 hours after nightfall for an urban scenario with elevated NO emissions and strong stability (scenario 9 in Table 1). We have chosen this case because it clearly illustrates the properties of the layers and their temporal behavior throughout the night (a more detailed discussion of the radical chemistry of scenario 9 will be given in section 3.6). After 1 hour a clear maximum of the reaction rate of up to \( 1.6 \times 10^9 \) molecules cm\(^{-3} \) s\(^{-1} \) develops in the lowest 20 m. As the night advances, this layer with enhanced reaction rate of NO + O3 moves upward, reaching a height between 5 and 40 m after 3 hours and between 10 and 70 m after 6 hours. Note that the overall rate decreases as the night proceeds (because [O3] rapidly
decreases in scenario 9). As will become clear later, the temporal behavior and the extent of the three layers depend predominantly on the vertical stability and the magnitude of the NO emissions.

[36] The vertical profile of the NO + O3 reaction rate allows us to distinguish the three chemical regimes in the NBL. The three layers are marked by different shades of gray in Figure 4.

[37] The unreactive ground layer, which occupies the lowest part of the NBL, is dominated by high concentrations of NO, which suppress significant levels of NO2 and O3. OH production is negligible because ozonolysis is unimportant, and RO2 is not formed in the absence of NO2 and O3. The ground layer is not always present in the NBL. At low NO emissions and weak stabilities, ozone destroyed by the freshly emitted NO near the ground is continuously replenished from aloft, and the ground layer does not form. This is, for example, the case in scenario 1, where ozone and NO are both present at the ground throughout the model run (Figure 2). At higher NO emission rates and stronger stabilities, as, for example, in scenario 9, the ground layer slowly grows in height after the continuously emitted NO has destroyed all O3 and NO3 near the ground. Ground layers can therefore frequently be observed in cities. In Figure 4 the ground layer is characterized by the near-zero NO + O3 reaction rate in the lower part of the NBL (dark gray zone). While it has not yet developed after 1 hour, the ground layer is ~3 m high after 3 hours and extends over the lowest 10 m after 6 hours.

[38] The upper layer is characterized by very low NO levels and is typically located at the upper end of the NBL. NO cannot reach this part of the NBL because it is converted to NO2 during its upward transport by the fast NO + O3 reaction. In the upper layer, OH is only produced by the ozonolysis of alkenes. Although RO2 is efficiently produced by NO2/O3 + VOC reactions, in particular in the lower part of the upper layer, it is only slowly converted into HO2 and OH in the absence of NO. Therefore the RO2 maximum discussed in section 3.2.1 is typically located in the lower part of the upper layer. The extent of the upper layer is controlled by the NO emission rate, stability, and time of night. In Figure 4 the upper layer is determined by the very low NO + O3 reaction rates at the top of the NBL (medium gray zone). Its lower boundary is at ~30 m after 1 hour. Because of the continuously emitted NO, the lower boundary of this layer increases to 70 m after 6 hours. In scenario 1 the ground layer extends from the ground to an altitude of ~15 m.

### 3.4. Steady State of ROx Radicals in the Reactive Mixing Layer

Because of their short lifetimes, we can establish equations for the pseudo steady state concentrations of RO2, HO2, and OH in the reactive mixing layer, which help in the interpretation of the various radical processes. We assume that the reaction with NO is the dominant loss path for RO2 and HO2 in the reactive mixing layer (Figure 3). This assumption is typically fulfilled for [NO] > ~100 ppt. The equations derived in this section are thus not valid in the upper layer or in very clean environments.

[41] The main sources of RO2 in the reactive mixing layer are (1) oxidation of VOCs by OH radicals (ΨRO2-OH-VOCs), (2) downward transport of RO2 from the upper layer (ΨRO2), and (3) in situ production by reactions of O3 and NO3 with VOCs (ΨRO2-O3-VOCs) (section 3.2.1). The pseudo steady state of RO2 can be expressed as

\[
[\text{RO2}] = \frac{\Psi_{\text{RO2}} + \Psi_{\text{RO2-NO3-VOCs}} + \Psi_{\text{RO2-O3-VOCs}} + \Psi_{\text{RO2-OH-VOCs}}}{k_{\text{RO2-NO}}}.
\]

[42] The main chemical sources of HO2 in the reactive mixing layer include reactions of RO2 radicals with NO (P_{\text{HO2-RO2-NO}} = k_{\text{RO2-NO}}[\text{RO2}][\text{NO}]) and the reaction of OH with CO (P_{\text{HO2-OH-CO}} = k_{\text{OH-CO}}[\text{OH}][\text{CO}]) (section 3.2.2). Another source of HO2 in the reactive mixing layer is in situ production by the reaction of O3 with VOCs (P_{\text{HO2-O3-VOCs}}). The HO2-NO2-HNO4 steady state (P_{\text{HO2-HNO4}}) also plays an important role as a source of HO2 in the reactive mixing layer, in particular at high traffic emissions and strong stabilities (see sections 3.5.1 and 3.5.2). The pseudo steady state of HO2 is therefore

\[
[\text{HO2}] = \frac{P_{\text{HO2-NO}} + P_{\text{HO2-O3-VOCs}} + P_{\text{HO2-OH-CO}} + P_{\text{HO2-HNO4}}}{k_{\text{HO2-NO}}}.
\]

[43] The only sources of OH in the reactive mixing layer are the reaction of HO2 with NO (P_{\text{OH-HO2-NO}} = k_{\text{OH-HO2-NO}}[\text{HO2}][\text{NO}]) and the ozonolysis of VOCs (P_{\text{OH-O3-VOCs}}) (section 3.2.3). Sinks of OH in the lower NBL include its reaction with VOCs, NO2, and CO. The pseudo steady state concentration of OH in the reactive mixing layer can therefore be expressed as

\[
[\text{OH}] = \frac{P_{\text{OH-HO2-NO}} + P_{\text{OH-O3-VOCs}}}{k_{\text{OH-NO}}[\text{VOCs}] + k_{\text{OH-NO2}}[\text{NO2}] + k_{\text{OH-CO}}[\text{CO}]}.
\]
The majority of RO2 radicals in the upper layer are formed by reactions of NO3 with VOCs leading to the formation of NOx. In scenario 1, downward mixing of RO2 is comparable to mixing over 2 m, 1 hour).

Equation (10) includes two known OH formation pathways. First, the production of RO2 radicals by photolysis of NO3 (with NO, other anthropogenic pollutants are also emitted at a different rate (see section 2 for the emission ratios). Also shown in Figure 5 are the profiles of NO and O3, which provide a link to our definition of the three-layer model.

3.5. Sensitivity Analysis

To determine the role of the various mechanisms influencing nocturnal RO chemistry, we performed a number of sensitivity studies. In particular, we investigated how the nocturnal RO chemistry reacts to changes in the emission rates of NO and VOCs, atmospheric stability, and ambient temperature. The parameters of the different scenarios are listed in Table 1. The variations of the vertical profiles of [RO2], [HO2], and [OH] and their most important production and loss rate changes under different conditions will be discussed with the help of equations (7)–(10) and the three-layer concept introduced in section 3.3.

3.5.1. Variation of the Traffic Emission Rate

Figure 5 shows the variation of the vertical profiles of [RO2], [HO2], and [OH] at NO traffic emission rates ranging from 1 x 10^10 to 30 x 10^10 molecules cm^-3 s^-1 3 hours after model start (scenarios 1–4 in Table 1). Together with NO, other anthropogenic pollutants are also emitted at a different rate (see section 2 for the emission ratios). Also shown in Figure 5 are the profiles of NO and O3, which provide a link to our definition of the three-layer model.

The vertical extent of the three layers introduced in section 3.3 strongly changes with the traffic emission rate. The ground layer is only formed in scenario 4 at high NO emissions, where it reaches an altitude of ~10 m (Figure 5). The reactive mixing layer occupies the lowest 5 m at low emissions (scenario 2) and increases to almost 30 m at medium-high emissions (scenario 3). Once the ground layer is formed, as in the high-emission scenario 4, the reactive mixing layer detaches from the ground, extending, for example, from ~10 to 100 m. In general, both the altitude and the vertical extent of the reactive mixing layer increase with increasing traffic emissions. Consequently, the lower boundary of the upper layer is displaced upward with increasing emission rates. In the case of high emissions (scenario 4) the upper layer starts at ~100 m. It is interesting to note that the small change in the traffic emission rates between scenario 3 and scenario 4 causes a drastic change in the behavior of the altitude dependence of nocturnal radical chemistry. This behavior can be explained by reaching a compensation point, at which downward transport cannot replenish ozone that is destroyed by NO emitted at the ground. Once this point is reached, a ground layer will form and will grow throughout the night, influencing the vertical distribution of all trace gases in the NBL.

The variations of the three RO2 profiles shown in Figure 5 follow the change of the vertical extent of the three layers with the traffic emission rate. As the altitude of the reactive mixing layer increases with increasing NO emission rates, the TO2 maximum, which is located in the lower
part of the upper layer (sections 3.2.1 and 3.3), is pushed upward, moving from ~10 m in scenario 2 to 90 m in scenario 4. The concentration of RO2 at the altitude of this maximum increases at higher traffic emissions because of the higher VOC levels, and thus $P_{\text{RO2-NO3+VOCs}}$ and $P_{\text{RO2-O3+VOCs}}$ increase.

Likewise, the altitudes of the HO2 concentration maximum in the upper part of the reactive mixing layer (sections 3.2.2 and 3.3) and the maximum of [OH] in the lower part of the reactive mixing layer (sections 3.2.3 and 3.3) increase with increasing traffic emissions. The extents of both maxima increase at higher emissions because the height of the reactive mixing layer increases. The behavior of [HO2] at the altitude of the HO2 maximum is dominated by two counteracting effects: an increasing loss rate $L_{\text{HO2-NO}}$ and an increasing production rate $P_{\text{HO2-RO2-NO}}$ at higher NO emissions (equation (8)). The magnitude of the HO2 maximum therefore changes little. OH concentrations at the height of the OH maximum decrease with increasing traffic emissions because [NO2] increases while [O3] and [NO3] decrease in the reactive mixing layer (equation (10)).

$3.5.2$. Variation of Atmospheric Stability

Figure 6 shows the vertical profiles of [RO2], [HO2], [OH], [NO], and [O3] 3 hours after model start at different atmospheric stabilities (scenario 6: neutral NBL, $K$ (10 m) = 1.0 m$^2$ s$^{-1}$; scenario 1: weak inversion, $K$ (10 m) = 0.3 m$^2$ s$^{-1}$; and scenario 5: strong inversion, $K$ (10 m) = 0.06 m$^2$ s$^{-1}$; see Table 1). In all three scenarios the reactive mixing layer extends over the lowest ~10 m of the NBL. A ground layer does not develop because of the low traffic emission rates, as can be seen by the high O3 levels at the ground (Figure 6).

The differences of the RO$_2$ profiles are caused by the increasing efficiency of vertical mixing at weaker stabilities. The RO$_2$ maximum in the upper layer broadens and becomes less pronounced at weaker stabilities. While, for example, the RO$_2$ maximum is limited to $15 \pm 5$ m in the strong inversion scenario 5, peaking at $\sim 90$ ppt, [RO$_2$] is elevated between 20 and $\sim 100$ m under the neutral conditions of scenario 6. This behavior can be explained by the weaker vertical gradients of VOCs at weaker stabilities (see section 3.1). Consequently, $P_{\text{RO2-NO3+VOCs}}$ decreases in the lower part of the upper layer, while it increases at higher altitudes for weaker stabilities. In the reactive mixing layer, [RO$_2$] increases at weaker stabilities because the downward flux of RO$_2$ from the upper layer (and thus $\Psi_{\text{RO2}}$ in equation (7)) is larger.

The vertical profiles of HO2 and OH do not significantly change with stability because the extent of the NO layer is similar in scenarios 1, 5, and 6. In the upper layer, [HO2] is only weakly dependent on stability because both $P_{\text{RO2-RO2-R0}}$ and $L_{\text{HO2-RO}}$ increase at weaker stabilities. Likewise, [OH] in the upper layer does not significantly change with stability because the changes in $P_{\text{OH-O3+VOCs}}$ and $L_{\text{OH-VOCs}}$ partly compensate each other. However, the peak concentrations of HO2 and OH in the reactive mixing layer increase at weaker stabilities (up to $1.9 \times 10^8$ molecules cm$^{-3}$ s$^{-1}$ in the neutral case) because of the higher downward flux of RO$_2$ and thus $\Psi_{\text{RO2}}$ (in equation (7)). In addition, the steady state concentration of OH in the reactive mixing layer is higher at weaker stabilities because $[\text{NO}_2]$ is decreasing (equation (10)). It is interesting to note that $P_{\text{HO2-HNO4}}$ in the lower part of the reactive mixing layer decreases at weaker stabilities. The lower $P_{\text{HO2-HNO4}}$ partly compensates the higher $\Psi_{\text{RO2}}$ and the lower OH loss rate by reaction with NO$_3$. Overall, the reactivity of the reactive layer increases at weaker stabilities.

$3.5.3$. Variation of Temperature

Figure 7 compares the 3 hour vertical profiles of [RO2], [HO2], [OH], [NO], and [O3] for temperatures at 10 m ranging from 275 to 305 K. In all three cases the reactive mixing layer extends over the lowest ~10 m of the NBL, and a ground layer does not develop. The temperature change has little effect on [NO] and [O3]. At increasing temperatures the concentrations of both NO$_3$ (because of a shift in the N$_2$O$_5$-NO$_3$ equilibrium [Geyer and Stutz, 2004]) and monoterpenes (because their emission rate increases) change has little effect on [NO] and [O3]. At increasing temperatures the concentrations of both NO$_3$ and HNO$_4$ in the lower part of the upper layer, while it increases at higher temperatures for weaker stabilities. While the RO$_2$ mixing ratio at 15 m in the 305 K scenario is 60 ppt, it exceeds 110 ppt in the 275 K scenario. The RO$_2$ maximum is also closer to the ground at higher temperatures, leading to higher RO$_2$ levels in the reactive mixing layer (because $\Psi_{\text{RO2}}$ and $P_{\text{RO2-NO3+VOCs}}$ increase). In the upper layer the increase of $P_{\text{RO2-NO3+VOCs}}$ is mostly compensated by the simultaneous increase of $L_{\text{RO2-NO3}}$, which is a dominant sink at this height. [RO$_2$] is thus only weakly temperature-dependent.

Figure 6. Vertical profiles of [RO$_2$], [HO$_2$], [OH], [NO], and [O$_3$] at different atmospheric stabilities in an urban case with moderate traffic emissions 3 hours after model start (scenarios 1, 5, and 6).
The concentration of HO\(_2\) increases with temperature in both the upper layer and the reactive mixing layer. The HO\(_2\) peak in the upper part of the reactive mixing layer is more pronounced at high temperatures. While the HO\(_2\) mixing ratio at 5 m is as high as 7 ppt at 305 K, it only reaches 2.5 ppt at 275 K. In the upper layer the higher [HO\(_2\)] at higher temperatures is caused by the higher NO\(_3\) levels, which lead to an enhanced \(P_{\text{HO}_2/\text{C}_0\text{RO}_2+\text{NO3}}\). The [HO\(_2\)] increases in the reactive mixing layer at higher temperatures are due to the higher HO\(_2\) production rate \(P_{\text{HO}_2/\text{C}_0\text{RO}_2+\text{NO}}\) (equation (8)).

No significant dependence of OH on temperature was found in the upper layer, since OH is predominantly produced by the weakly temperature-dependent ozonolysis of anthropogenic alkenes \(P_{\text{OH/\text{C}_0\text{O}_3+\text{VOCs}}}\). However, the peak OH concentration in the lower part of the reactive mixing layer is as high as \(1.9 \times 10^6\) molecules cm\(^{-3}\) at 305 K, while [OH] only reaches \(1.0 \times 10^6\) molecules cm\(^{-3}\) at 275 K (Figure 7). In the lower part of the reactive mixing layer, [OH] increases with temperature because both \(P_{\text{RO}_2/\text{C}_0\text{NO}_3+\text{VOCs}}\) and \(\Psi_{\text{RO}_2}\) increase (equation (10)).

### 3.6. High-Emission Stable Urban Case

In polluted urban areas a fast and complete destruction of ozone at the ground is often observed during the night [e.g., Lee et al., 2003]. This O\(_3\) depletion can be interpreted as the fast formation of the unreactive ground layer. It occurs if two conditions are met: (1) a strong atmospheric stability, which prevents ozone from being transported from aloft and replenishing lost O\(_3\) at the ground, and (2) high traffic emissions of NO, which lead to a high loss rate of O\(_3\) by its reaction with NO (section 3.3). In this section we investigate the vertical profiles of RO\(_x\) radicals in such a high-emission stable urban case (scenario 9 in Table 1). This scenario was also used in section 3.3 to explain the three-layer concept of the NBL.

In the high-emission/high-stability case the levels of NO, NO\(_3\), and anthropogenically emitted VOCs are considerably higher than in scenario 1. After 3 hours, for example, both [NO] (Figure 8) and [NO\(_2\)] (not shown) reach \(\sim 120\) ppb close to the ground. In contrast, ozone and NO\(_3\) levels rapidly decrease during the night. Consequently, a ground layer begins to form after 1 hour, increasing in height as the night proceeds and covering the lowest \(\sim 15\) m after 6 hours (see also Figure 4). This ground layer is characterized by very low O\(_3\) levels, as can be seen in Figure 8. The growing ground layer slowly pushes the reactive mixing layer upward. While the reactive mixing layer is located in the lowest 20 m after 1 hour, it spans from 15 to 60 m after 6 hours.

Figure 8 shows vertical profiles of [RO\(_2\)], [HO\(_2\)], and [OH] during the first 6 hours of the night in this scenario. Similar to the weakly stable urban case discussed in sections 3.1–3.5, a layer with elevated RO\(_2\) levels develops in the lower part of the upper layer. As already discussed in
Similar to the weakly stable urban case, a peak of the OH concentration develops in the lower part of the reactive mixing layer. After 1 hour, ~6 × 10^5 molecules cm^{-3} s^{-1} of OH are present in this layer. With the reactive mixing layer the altitude of the OH maximum increases during the night. As the extent of the reactive mixing layer increases, the OH maximum broadens as it moves upward through the NBL. In addition, the increasing NO2 concentrations during the night lead to a decrease of [OH] at the height of its maximum.

### 3.7. Rural Low-Emission Case

In this section the vertical profiles of ROx radicals in a rural low-emission case (scenario 10 in Table 1) are investigated. The rural conditions are characterized by the absence of anthropogenic emissions; low initial levels of NO2, O3, and anthropogenic VOCs but high initial levels of biogenic VOCs; and high emission rates of monoterpenes. Our discussion in section 3.4, including equations (7)–(10), is therefore not always applicable. We used an average emission rate of monoterpenes of 10 × 10^6 molecules cm^{-3} s^{-1} (for class API at 290 K) in this scenario.

In the rural case the concentrations of NO and NO2 are considerably lower than in the urban cases (NO is <1 ppb at the ground; NO2 is 2 ppb). In addition, NO is only emitted from the ground and not, as in the urban cases, between 0.1 and 1 m. The missing traffic NO sources have an influence on the trace gas gradients in the lowest meter of the atmosphere. NO, for example, shows a strong gradient in the lowest meter, which is caused by the slow transport and the simultaneous reaction with O3, which is not observed in urban scenarios (Figure 9). In the rural scenario, NO does not reach altitudes above 5 m. The initial ozone level of ~40 ppb does not significantly change during the night, and [O3] develops a weak positive gradient, mostly due to dry deposition. NO3 and N2O5 develop positive gradients, which are caused by the high monoterpane levels in the lower NBL. Both NO3 and N2O5 are lower in the rural case than in the urban scenarios ([NO3] is around 5 ppt). Monoterpenes develop negative gradients, which are caused by their reactions with NO3 and O3 [Geyer and Stutz, 2004]. Throughout the night the reactive mixing layer is located in the lowest meter of the NBL. A ground layer does not develop.

Vertical profiles of [RO2], [HO2], and [OH] for a rural case (scenario 10) are shown in Figure 9. The ROx profiles change very little throughout the night. Only at the beginning of the night, when VOCs emitted during the day are still oxidized, are [RO2] and [HO2] slightly elevated. Similar to the urban cases, all three RO2 radicals develop pronounced concentration maxima at a specific altitude. The RO2 concentration is highest at 20 m altitude. Below this altitude, [RO2] decreases toward the ground because of the elevated L_{RO2→NO} rate in the lowest meter. Above 20 m, [RO2] decreases with increasing altitude because of the decreasing concentrations of monoterpenes, which are oxidized during their upward transport. The maximum RO2 mixing ratio decreases from 65 ppt after 1 hour to 55 ppt 5 hours later. In general, the RO2 levels in the NBL depend on the monoterpane emission rate (not shown here), because P_{RO2→O3+VOCs} increases with the monoterpane levels. In addition, the initial levels of isoprene at night...
play a role. For example, a fivefold increase of initial isoprene increases RO2 mixing ratios by ~20%. $P_{RO2-NO3-VOCs}$ depends less on the monoterpene emission rate and initial isoprene levels because [NO3] simultaneously decreases at higher monoterpene and isoprene concentrations. Downward transport acts as the main source of RO2 in the reactive mixing layer.

Both HO2 and OH have a strong maximum in the reactive mixing layer, which occupies the lowest meter of the NBL. Close to the ground, [OH] can reach levels of several million molecules per cubic centimeter. These maxima are formed by the elevated reaction rates of RO2 and HO2 with NO, which is emitted from the ground. The strong vertical [OH] gradient in the lowest meter (Figure 9) is not observed in urban cases, which also include emission between 0.1 and 1 m. Because [RO2] increases in the reactive mixing layer at higher monoterpene emission rates and higher initial isoprene concentrations, [HO2] and [OH] also increase because of the increase of $P_{HO2-RO2-NO}$ and $P_{OH-HO2-NO}$. In the upper layer, [HO2] changes little with altitude and is predominantly produced by ozonolysis of monoterpenes and isoprene and self reactions of RO2 radicals. The HO2 mixing ratio in the upper layer depends little on monoterpene emissions and isoprene concentrations because the increase of $P_{HO2-RO2}$ and $P_{HO2-RO2}$ is compensated by the simultaneous increase of $L_{RO2-RO2}$. An OH concentration of ~10^5 molecules cm^{-3} is maintained by the ozonolysis of monoterpenes and isoprene in the upper layer. The OH concentration in the upper layer increases at higher monoterpene emission rates and initial isoprene because of higher $P_{OH-RO3-VOCs}$.

Our model is based on the original RACM mechanism by Stockwell et al. [1997]. However, we also performed model calculations with an updated RACM version that includes the isoprene oxidation scheme proposed by Geiger et al. [2003]. For the initial isoprene levels used in our rural scenario (case 10), differences in the concentrations of O3, NO, and NO3 are negligible between the schemes. NO2 concentrations change near the ground by <5%. The shape of the vertical profiles of all three RO2 radicals is similar in both cases (Figure 9). However, the mixing ratios of RO2 are higher by ~20% with the new isoprene oxidation scheme. HO2 levels above 3 m altitude are lower with the updated RACM mechanism, while the OH concentration changes are small. The higher RO2 concentrations lead to an increase of both HO2 and OH of ~20% below 3 m, where RO2 is mixed with NO. The new scheme by Geiger et al. [2003] changes the radical levels in our model slightly. However, the general behavior and the various chemical transport mechanisms are reproduced with the new isoprene oxidation scheme.

Our investigation of the nocturnal chemistry in rural areas illustrated that similar mechanisms found in urban areas are active. However, the lack of NO emissions restricts the reactive mixing layer to the lowest few meters above the ground, where NO is still elevated. Our sensitivity analysis regarding the emissions of monoterpenes and the concentration of isoprene shows that nocturnal rural radical chemistry is dependent on the concentration of these species. Thus factors such as type of vegetation and temperature that influence the concentration of the biogenic VOCs have to be considered for more specific model calculations.

3.8. Comparison of the Model Results With Field Data

It is difficult to compare the modeled vertical profiles of [RO2], [HO2], and [OH] with measured data at night because no measurements of the vertical profiles of RO2 radicals have been performed thus far. Most reported measurements were taken at 3–10 m height. The model results show that, in particular, the RO2 mixing ratios develop a strong gradient in the lowest ~20 m of the atmosphere, and small changes in stability and emission rates can lead to considerable changes in [RO2] at 10 m. Therefore we can only compare the general levels predicted by the model in the lower NBL with the field observations.

Measurements of RO2 in the atmosphere were thus far almost exclusively performed in rural areas [Cantrell et al., 1996a, 1996b, 1997; Carlaw et al., 1997; Geyer et al., 2003; Holland et al., 2003; Hu and Stedman, 1995; Kanaya et al., 1999; Mihelic et al., 1993, 2003; Monks et al., 1996]. The one-dimensional model predicts ~50 ppt of RO2 at 10 m altitude in the rural case in Figure 9. However, this level strongly depends on the monoterpene emission rate. While <30 ppt of RO2 are modeled for an API emission rate of 3 × 10^6 molecules cm^{-3} s^{-1}, up to 90 ppt can be present at a rate of 30 × 10^6 molecules cm^{-3} s^{-1}. These modeled RO2 levels are in the range of observed data, for example, by Mihelic et al. [1993], who measured up to 40 ppt RO2 on a mountain in Germany. In a rural area near Berlin, Germany, Geyer et al. [2003] observed 6 ppt of RO2 at night. The monoterpene levels of 15–25 ppt measured at this site were, however, considerably lower than the levels modeled in scenario 10, thus causing the lower RO2 concentration.

The general levels of HO2 and OH radicals predicted by the NCAT model for the various cases are in good agreement with the few observations in the NBL. For example, measurements near Berlin shortly before sunrise found that HO2 was often on the order of 4 ppt, while OH peaked at 1.9 × 10^5 molecules cm^{-3} [Geyer et al., 2003]. These values are on the order of the model results of scenario 10 at 10 m altitude (Figure 9).

Although a layer of elevated OH concentrations near the ground is predicted for all scenarios discussed in this study, we cannot assess whether the recent observations of ~10^6 molecules cm^{-3} of OH at night above a forest and in New York City [Faloona et al., 2001; Ren et al., 2003] could be reproduced by our model without explicit calculations for the conditions encountered during these measurements.

The OH levels modeled in our rural scenario above 3 m are lower than the concentrations of ~2 × 10^6 molecules cm^{-3} and ~2 × 10^5 to 10 × 10^5 molecules cm^{-3} found by Makar et al. [1999] and Sillman et al. [2002], respectively. In addition, our HO2 levels in this case are also lower. This discrepancy is most likely caused by a different choice in emission scenarios, since the studies of Makar et al. [1999] and Sillman et al. [2002] were both performed for forested areas with very high biogenic hydrocarbon emissions. It should be noted that the shape of vertical OH and HO2 profiles by Makar et al. [1999]
shows only weak altitude dependence above 5 m altitude, in agreement with our results. Below 5 m the assumption of a flat surface in our case leads to a different behavior than in the case of Makar et al. [1999].

4. Oxidation of VOCs and NO2 by OH at Night

The hydroxyl radical is known to be the main oxidant of VOCs and NO2 during the day. At night, oxidation of pollutants by OH has thus far been mostly neglected. In this section we investigate the role of nocturnal OH in the removal of VOCs and NO2.

Table 2 summarizes the oxidation rates of VOCs and NO2 by nighttime OH, averaged over the lowest 100 m of the NBL for the cases discussed in section 3, 3 hours after model start. In addition to the oxidation rates the relative contributions of nighttime OH compared with NO3 and O3 are shown. Reaction rates of OH + VOCs between 35 ppt h⁻¹ in the rural case (scenario 10) and 1095 ppt h⁻¹ in the weakly stable/high-emission scenario 4 were found. Nighttime OH contributes 13–46% to the total VOC oxidation at night. Compared with the oxidation rates of VOCs by OH during the day, which often exceed 1 ppb h⁻¹ [Crosley, 1997; Eisele et al., 1997; Geyer et al., 2001; Goldan et al., 1997; Stroud et al., 2001; Tan et al., 2001], the oxidation rates by OH during the night are low but not negligible.

The single most important parameter controlling the contribution of the OH oxidation to the VOC removal is the emission rate of NO and other anthropogenic pollutants. The OH-induced VOC oxidation rate increases by a factor of 7 between low-emission scenario 2 and high-emission scenario 4. The relative contribution of nighttime OH to the nocturnal oxidation does, however, only change by a few percent, since the NO3 + VOC and O3 + VOC reaction rates also increase. Higher temperatures lead to a slightly higher OH + VOC reaction rate because the emission rates of biogenic VOCs increase. The relative contribution of OH is highest at cold temperatures (30%) because the contribution of NO3 decreases with temperature. The degree of atmospheric stability has no strong influence on the role of nighttime OH as a VOC oxidant.

In the rural cases the contribution of OH to the nocturnal VOC oxidation is considerably lower. The reaction rates are more than 1 order of magnitude below the rates in the urban cases. The low contribution can be explained by the fact that nighttime OH predominantly oxidizes anthropogenic VOCs, while the most abundant VOC species in the rural cases are biogenic monoterpenes, which are also oxidized by NO3 and O3.

The results show that the contribution of nighttime OH to the VOC oxidation depends on the VOC mixture. In particular, in a case with high levels of alkanes or aldehydes, the hydroxyl radical can play a key role as an oxidant at night.

Nighttime OH can also contribute to NO2 removal from the atmosphere by the oxidation of NO2 into HNO3 (followed by deposition of HNO3). An oxidation rate of NO2 by reaction with OH in the range of 22–585 ppt h⁻¹ is predicted by the model in the urban scenarios (Table 2). Compared with other reactions, in particular, the hydrolysis and aerosol uptake of N2O5 [Geyer and Stutz, 2004], nighttime OH contributes only a few percent to the NO2 loss in the NBL under normal conditions. Compared with the reaction of OH + NO3 reaction rate during the day, which can be as high as 7 ppb h⁻¹ at [OH] = 10⁷ molecules cm⁻³ and [NO3] = 20 ppb [Donahue et al., 1997], NO2 oxidation by nighttime OH is less important. The reaction rate of OH + NO3 shows a clear dependence on the NO emission rate and is more than an order of magnitude larger in high-emission scenario 4 than in scenario 2. Temperature and atmospheric stability have a minor influence on this reaction. In the rural cases, lower reaction rates of OH + NO3 were found (~9 ppt h⁻¹). The relative contribution of nighttime OH to the NO2 removal increases with the monoterene emission rate because the levels of NO3 and N2O5 decrease simultaneously.

5. Conclusions

A vertically highly resolved one-dimensional chemical transport model based on the RACM gas phase chemistry mechanism was applied to investigate the development of vertical profiles of peroxy radicals and OH in the nocturnal boundary layer. Our model results show that the vertical profiles of organic peroxy radicals, RO2, show a maximum in the lower part of the NBL in all scenarios we investigated. The strong positive gradient below the maximum is caused by the high loss rate of RO2 through its reaction with NO close to the ground. Above the maximum, [RO2] slowly decreases with altitude because the RO2 production by reactions of NO3 and O3 with unsaturated VOCs decreases. In all scenarios the reaction of NO3 with monoterpenes is the most important net RO2 source at
night. Hydroperoxy radicals, HO2, develop a similar profile to RO2. The maximum is, however, located closer to the ground. The positive gradient of HO2 below this maximum is caused by the fast removal of HO2 by reaction with NO. Above the maximum, [HO2] decreases mostly because the HO2 production by RO2 + NO reactions decreases. The concentration of the hydroxyl radical, OH, is \(10^6\) molecules cm\(^{-3}\) in the upper part of the NBL. However, in a layer close to the ground a high concentration maximum of \(\sim 10^6\) molecules cm\(^{-3}\) can develop. These high nighttime levels of OH are caused by the maximum of the reaction rate of HO2 and NO in this layer. Nighttime OH can significantly contribute to the removal of VOCs. In the cases discussed in this paper, 17–43% of the VOC oxidation is caused by OH at night. The conversion of NO2 into HNO3 by nighttime OH is negligible.

[78] To simplify the description of the altitude-dependent RO2 chemistry in the NBL, we propose to distinguish three chemical regimes on the basis of their RO2 chemistry and OH production rates. The regimes can be easily distinguished by using the NO + O3 formation rate as an indicator.

[79] 1. The ground layer near the surface is defined by high levels of NO, which suppress the presence of NO3 and O3, reducing the NO + O3 formation to near zero. All radical levels in this layer are low, and radical chemistry is basically inactive. The ground layer only forms when the destruction of O3 by NO emissions at the ground surpasses the replenishment of ozone through downward transport.

[80] 2. The upper layer at the top of the NBL is characterized by high levels of NO3, O3, and organic peroxy radicals but negligible NO concentrations. Here VOCs are oxidized by NO3 and O3, but the peroxy radicals are only slowly converted into OH radicals. OH is mostly produced by the ozonolysis of alkenes. Again, the NO + O3 rate is very low because of the low NO levels. The nocturnal RO2 maximum typically develops in the lower part of the upper layer.

[81] 3. The reactive mixing layer is located between the ground layer and the upper layer. In this height interval, NO from the ground layer and NO3, O3, and RO2 from the upper layer are mixed together. It is important to realize that in this layer the otherwise chemically unlikely simultaneous presence of RO2, NO3, and NO is maintained by vertical mixing. In addition to their downward transport, organic peroxy radicals are produced by NO3 + VOC and O3 + VOC reactions. RO2 is rapidly converted into HO2 and OH by reactions with NO. This fast radical propagation chain leads to high HO2 and OH production. The concentration maxima of HO2 and OH are located in the reactive layer. The reactive mixing layer is thus the height interval with the most active radical chemistry in the NBL.

[82] Our results illustrate a number of unique chemical transport mechanisms in the NBL that have thus far not been discussed in the literature:

[83] 1. Vertical transport of RO2 radicals can play a crucial role for nocturnal chemistry. This transport is driven by the RO2 concentration gradient, which is formed by high RO2 production rates through the NO3/NO + VOC reactions in the lower part of the upper layer, and destruction of RO2 through its reaction with NO in the reactive mixing layer. Downward mixing of RO2 acts as a sink for RO2 above the NO-rich layer and as an important source close to the ground. This mechanism is important in all scenarios we investigated but in particular in scenarios with high monoterpene concentrations and weak stability.

[84] 2. Vertical transport of HNO4, followed by its thermal decay, also often acts as an important source of HO2 and thus indirectly of OH, near the ground. A positive vertical gradient of HNO4 is formed through the destruction of HO2 by NO near the ground that reduces [HNO4] compared with its much higher pseudo steady state value aloft. This gradient leads to a downward transport of HNO4, which then acts as an HO2 source near the ground. This mechanism increases in importance with the degree of pollution and the vertical stability in the atmosphere. It is particularly important in urban environments.

[85] These two chemical transport mechanisms, in combination with purely chemical OH formation mechanisms, such as the ozonolysis of VOCs, can lead to significant amounts of OH in the reactive mixing layer. Further studies are necessary to expand our somewhat idealized model calculations to more realistic conditions. In addition, it would be desirable to test our results with field experiments that study the vertical distribution of radical species. The results of this paper and of previous work [Geyer and Stutz, 2004] clearly demonstrate the necessity of a one-dimensional approach with sufficient vertical resolution for both experimental and modeling studies of nocturnal chemistry.

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References


Figure 3. Vertical profiles of chemical rates and the rate of change by vertical transport of RO₂, HO₂, and OH 3 hours after model start for scenario 1.