Influence of meteorology and anthropogenic pollution on chemical flux divergence of the NO-NO$_2$-O$_3$ triad above and within a natural grassland canopy

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Abstract

The detailed understanding of surface-atmosphere exchange fluxes of reactive trace gases species is a crucial precondition for reliable modeling of processes in atmospheric chemistry. Plant canopies significantly impact the atmospheric budget of trace gases. In the past, many studies focused on taller forest canopies or crops, where the bulk plant material is concentrat-
ed in the uppermost canopy layer. However, within grasslands, a land-cover class that globally covers vast terrestrial areas, the canopy structure is fundamentally different, as the main biomass is concentrated in the lowest part of the canopy. This has obvious implications for aerodynamic in-canopy transport, and consequently also impacts on global budgets of key species in atmospheric chemistry such as nitric oxide (NO), nitrogen dioxide (NO₂) and ozone (O₃).

This study presents for the first time a comprehensive data set of directly measured in-canopy transport times and aerodynamic resistances, chemical timescales, Damköhler numbers, trace gas and micrometeorological measurements for a natural grassland canopy (canopy height = 0.6 m). Special attention is paid to the impact of contrasting meteorological and air chemical conditions on in-canopy transport and chemical flux divergence. Our results show that the grassland canopy is decoupled throughout the day. In the lowermost canopy layer, the measured transport times are fastest during nighttime, which is due to convection during nighttime and a stable stratification during daytime in this layer. The inverse was found in the layers above. During periods of low wind speed and high NOₓ (NO+NO₂) levels, the effect of canopy decoupling on trace gas transport was found to be especially distinct. The aerodynamic resistance in the lowermost canopy layer (0.04–0.2 m) was around 1000 s m⁻¹, which is as high as values from literature determined previously for the lowest meter of an Amazonian rain forest canopy. The aerodynamic resistance representing the bulk canopy was found to be more than 3–4 times higher as than in forests. Calculated Damköhler numbers (ratio of transport and chemical timescales) suggested a strong flux divergence for the NO-NO₂-O₃ triad within the canopy during daytime. At During that time, the timescale of NO₂ plant uptake by plants ranged from 90 to 160 s and was the fastest relevant timescale, i.e. faster than the reaction of NO and O₃. Thus, our results clearly reveal that grassland canopies of
similar structure have exhibit a strong potential to retain soil emitted NO by due to oxidation and subsequent uptake of NO₂ by the plants. Furthermore, a photo-chemical O₃ production was observed above the canopy, which was attributed to a deviation from the NO-NO₂-O₃ photostationary state by a surplus of NO₂ due to oxidation of NO by e.g., peroxy radicals, which resulted from a surplus of NO₂ from the NO-NO₂-O₃ photostationary state. The O₃ production was one order of magnitude higher during high NOₓ than during low NOₓ periods and resulted in an underestimation of the O₃ deposition flux measured with the EC method underestimation, which was observed for the first time.

1 Introduction

Nitric oxide (NO) and nitrogen dioxide (NO₂) play a crucial role in air chemistry since as they act as key catalysts for ozone (O₃) production and are therefore involved in the generation of hydroxyl radicals (OH) (Crutzen, 1973). The most significant tropospheric source of O₃ is initiated by photochemical dissociation of NO₂ and subsequent reaction of the oxygen (O) atom with molecular oxygen:

\[
\text{NO}_2 + \text{hv} (\lambda < 420 \text{ nm}) \rightarrow \text{NO} + \text{O}^3\text{P} \quad \text{(R1)}
\]

\[
\text{O}^3\text{P} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \quad \text{(R2)}
\]

When in case O₃ is present, it may oxidize NO and re-form NO₂:

\[
\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2 \quad \text{(R3)}
\]

In the absence of additional reactions, R1–R3 represent a null cycle. Besides R1–R3, NO is oxidized by peroxy radicals (HO₂+RO₂), which constituting constitutes an additional important net O₃ production pathway in the troposphere (Warneck, 2000).
Dry deposition to terrestrial surfaces, especially to plant canopies, is an important sink for tropospheric O₃ and NO₂. The uncertainties of dry deposition estimates are substantially higher for NO₂, because its net ecosystem exchange can be bi-directional depending on the ambient NO₂ levels (Lerdau et al., 2000). O₃ instead is exclusively deposited to surfaces. In contrast, NO is known to be mainly net emitted from nearly all soil types. Biogenic NO soil emissions contribute about 20% to the global NOₓ (NO+NO₂) emissions (IPPC, 2007, 2013), highlighting the need of careful, detailed investigations on NOₓ soil-atmosphere exchange.

A major challenge for studies investigating surface-atmosphere exchange fluxes of these reactive trace gases is the presence of plant canopies. These significantly modify the turbulent properties of the surface and thus alter trace gas exchange fluxes. Most previous studies focused on taller canopies such as forests. However, grassland canopies represent a highly important land cover class covering globally 41% and Europe-wide 19% of the terrestrial land surface (Suttie et al., 2005; Kasanko et al., 2011). In contrast to forests, grasslands feature the main bulk plant area density near the soil (e.g., Ripley and Redman, 1976; Jäggi et al., 2006), accompanied with mean distances between plant elements of only some millimeters (Aylor et al., 1993). Organized coherent structures govern turbulence dynamics within and above plant canopies (Finnigan, 2000). The mean in-canopy transport is slower than above the canopy (e.g., Nemitz et al., 2009). This modification of in-canopy transport has important implications for global atmospheric chemistry. Plant canopies and the soil below are biologically actively emitting and taking up reactive trace gases, and they-conditions within canopies may provide sufficient time for fast chemical reactions to occur within the canopy (Nemitz et al., 2009). Subsequently, they modify surface exchange fluxes (e.g., Rinne et al., 2012). For instance, ammonia can be released by a part of the canopy and taken up by another (Nemitz et
al., 2000; Denmead et al., 2007). In addition, recapturing of NO\textsubscript{2} originating from biogenic soil NO emissions after reaction with O\textsubscript{3} within plant canopies (Rummel et al., 2002) is accounted for in global models by a so-called canopy reduction factor for NO\textsubscript{x} (Yienger and Levy, 1995). However, these estimates are based on only one single experiment in an Amazonian rain forest (Bakwin et al., 1990), and a subsequent model analysis (Jacob and Wofsy, 1990). Canopy reduction for grasslands and other ecosystems was not experimentally studied up to now. Consequently, the contrasting canopy structure of grassland and forest ecosystems highlights the need for a detailed analysis and an evaluation of the suggested NO\textsubscript{x} canopy reduction factor of e.g. 64\% suggested by Yienger and Levy (1995) for temperate grassland.

Net ecosystem exchange fluxes are typically measured at a certain height above the canopy. They rely on the constant flux layer assumption (e.g., Swinbank, 1968), which however, may be violated for reactive trace gases within or just above the vegetation. To assess the potential chemical divergence of exchange fluxes, the Damköhler number (DA) has commonly been applied (e.g., Rinne et al., 2012). DA is calculated as the ratio of the transport time (τ\textsubscript{tr}) and the characteristic chemical timescale (τ\textsubscript{ch}):

\[
DA = \frac{\tau_{tr}}{\tau_{ch}} \tag{1}
\]

Hence, DA above unity indicates that chemical reactions occur significantly faster than the transport (flux divergence), whereas DA smaller than 0.1 indicate the reverse case. The range in-between is commonly addressed as a critical range, where an impact of chemistry cannot be excluded (Stella et al., 2013).

In this paper, we present directly measured transport times, chemical timescales and corresponding Damköhler numbers for three layers above and within a natural grassland canopy.
under contrasting meteorological and air chemical conditions. For the first time, such a comprehensive analysis involving trace gas and micrometeorological measurements is made for a grassland canopy. Furthermore, the consequences of in-canopy processes for NO$_x$ canopy reduction and simultaneously measured O$_3$ deposition fluxes will be discussed.

2 Material and Methods

2.1 Site description

We performed an intensive field experiment from July to September 2011 at the estate of the Mainz-Finthen Airport in Rhineland-Palatinate, Germany (further details given in Plake and Trebs, 2013; Plake et al., 2014; Moravek et al., 2014). The vegetation at the site was nutrient-poor grassland with a mean canopy height ($h_c$) of 0.6 m and a leaf area index (LAI) of 4.8 m$^2$ m$^{-2}$. A list of species and an LAI profile are given in Plake et al. (2014), with the latter indicating a high biomass density below 0.2 m corresponding to 85% of the total LAI. Topographically located on a plateau 150 m above the Rhine valley, the site is situated about 9 km south-west of the city center of Mainz. The site was surrounded by villages and motorways in a distance of 2 to 6 km and 4 to 15 km, respectively. The surrounding area was mainly characterized by agricultural use for vineyards, orchards and crops. The fetch was largest in south-western direction without significant anthropogenic pollution sources.

2.2 Experimental setup

A vertical Thoron (Tn) profile system was operated at $z_1 = 0.04$ m, $z_2 = 0.2$ m and $z_3 = 0.8$ m for the direct determination of transport times (for details see Plake and Trebs, 2013). Vertical profiles of NO, NO$_2$, O$_3$ and CO$_2$ were measured at $z_1$, $z_2$, $z_3$ and additionally at $z_4 = 4.0$ m by a system described in detail by Plake et al. (2014). Briefly, NO was measured by detection
of the chemiluminescence produced during the reaction of NO and O$_3$ (TEI 42iTL Thermo Scientific, Waltham, USA). NO$_2$ was photolytically converted to NO by exposure of the sample air to a Blue Light Converter (BLC, Droplet Measurement Technologies, Boulder, USA). O$_3$ mixing ratios were measured with a UV-absorption analyzer (TEI-49i, Thermo Scientific, Waltham, USA). The efficiency of the photolytic conversion of NO$_2$ to NO was determined by a back titration procedure involving the reaction of O$_3$ with NO using a gas phase titration system (SYCOS K-GPT, Ansysco GmbH, Karlsruhe, Germany). Details on the sampling schedule and time resolution of the trace gas profiles system are described in Plake et al. (2014).

This study is based on simultaneous operation of both vertical profile systems at identical heights and, thus, focuses on the period from 19 August to 26 September 2011 when both systems were operational. Vertical profiles of temperature (HMT337, Vaisala, Helsinki, Finland), wind speed and direction (WS425, Vaisala, Helsinki, Finland) were installed at 0.2 m, 0.8 m, 1.5 m, 2.5 m, 4.0 m. Soil temperature (107L, Campbell Scientific Inc., Logan, USA) was measured at -0.02 m. Global radiation ($G$) and the NO$_2$ photolysis frequency ($j_{NO_2}$) were measured at a height of 2.5 m with a net radiometer (CNR1, Kipp&Zonen, Delft, Netherlands), and a filter radiometer (Meteorology Consult GmbH, GlashüttenKönigstein, Germany), respectively. The data of temperature, wind and radiation were recorded by a data logger (CR3000, Campbell Scientific) every 10 seconds. A three-dimensional sonic anemometer (CSAT-3, Campbell Scientific) placed at $z_{ref} = 3.0$ m measured 3D wind and temperature at 20 Hz and the data were recorded by a CR3000 data logger. The friction velocity ($u_*$) and stability functions ($z/L$) were computed using the TK3 software (see Mauder and Foken, 2011). Eddy covariance fluxes of O$_3$ were simultaneously measured and are described in detail by Plake et al. (2014).
2.3 Theory

The data analysis was carried out for three individual layers \((L_{1-3})\), which were named in ascending order starting at the soil surface. Hence, \(L_1\) was the lowermost canopy layer between the corresponding measurement heights \(z_{1-2} (\Delta z(L_1) = 0.16 \text{ m})\), \(L_2\) the upper canopy layer between \(z_{2-3} (\Delta z(L_2) = 0.6 \text{ m})\), and \(L_3\) the layer above the canopy between \(z_3\) and \(z_{\text{ref}} (\Delta z(L_3) = 2.2 \text{ m})\). As shown in Plake et al. (2014) the vertical trace gas gradients between \(z_{\text{ref}}\) and \(z_4\) were negligible, allowing the use of mixing ratios measured at \(z_4\) for \(L_3\).

2.3.1 Chemical timescales

The overall chemical timescale \(\tau_{ch}\) (in s) of the NO-NO\(_2\)-O\(_3\) triad (Lenschow, 1982) was calculated for each layer \((L_i, i = 1, 2, 3)\) as:

\[
\tau_{ch}(L_i) = \frac{2}{\sqrt{J_{NO_2}(L_i)^2 + k_3(L_i)^2 + k_3(L_i)^2(N_{O_3}(L_i) + N_{NO}(L_i)) + 2J_{NO_2}(L_i)k_3(L_i)(N_{O_3}(L_i) + N_{NO}(L_i) + 2N_{NO_2}(L_i))}}\]

(2)

where \(N_{O_3}\), \(N_{NO}\) and \(N_{NO_2}\) are the number densities (in molecules cm\(^{-3}\)) of O\(_3\), NO and NO\(_2\) for \(L_{1-3}\), and \(k_3\) the reaction rate constant of R3 (in cm\(^3\) molecule\(^{-1}\) s\(^{-1}\)) according to Atkinson et al. (2004). Geometric means of the number densities at \(z_{1-4}\) were used in Eq. 2 to account for non-linear profiles (e.g., \(N_{NO}(L_1) = \sqrt{N_{NO}(z_1) \cdot N_{NO}(z_2)}\)).

Equation 2 gives the chemical time scale of reactions R1 and R3 derived from the O\(_3\) chemical-budget equation, i.e., considering only the reactions between O\(_3\), NO and NO\(_2\) and not taking into account reactions of other compounds (e.g., peroxy radicals and VOCs). It is defined as the time at which the mixing ratio of one of the compounds significantly changes from its initial value when reacting with the other ones. It can also be seen as the time re-
quired for reaching a new photostationary state following a change in O₃, NO or NO₂ mixing ratios, or the reaction rate constants \( j_{NO_2} \) and \( k_3 \) (see Ganzeveld et al., 2012). The underlying assumptions are:

- **only source and sink terms of the “triad” are considered, which means other reactions (e.g. RO₂ + NO) are not included.**
- covariance terms and other budget terms i.e. horizontal and vertical advection, flux divergence and change in O₃ mixing ratio \( d[O_3]/dt \) are neglected.

### 2.3.2 NO₂ photoysis within the canopy

The data gaps in the measured time series of \( j_{NO_2} \) (in s⁻¹) above the canopy were filled using the parameterization of \( j_{NO_2} \) as a function of \( G \) (in W m⁻²) by Trebs et al. (2009). This approach was also used to parameterize in-canopy \( j_{NO_2} \) from a vertical in-canopy profile of \( G \).

The latter was calculated as function of the LAI profile using the method of Monsi and Saeki (1953):

\[
G(LAI) = G_0 \cdot \exp(-k_{ex}LAI)
\]

where \( G_0 \) (in W m⁻²) is the above-canopy \( G \) and \( k_{ex} \) is the dimensionless extinction coefficient of the canopy. In this study, the extinction coefficient of barley (\( k_{ex} = 0.69 \) by Monteith and Unsworth (1990)) was used. First \( G(LAI) \) was deduced and then converted into \( j_{NO_2} \). Finally, geometric means of \( j_{NO_2} \) were calculated for \( j_{NO_2}(L_{1-3}) \).

### 2.3.3 Transport times

For \( L_3 \), height integrated transport times \( \tau_{tr}(L_3) \) (in s) were derived by multiplying the aerodynamic resistance \( (R_a(L_3)) \) (e.g., Hicks et al., 1987; Erisman et al., 1994) with the layer thickness \( (\Delta z(L_3)) \) (cf. Stella et al., 2013):
\[
\tau_{tr}(L_3) = R_a(L_3) \cdot \Delta z(L_3)
\]  
(4)

\[
R_a(L_3) = \frac{1}{\kappa u_*} \left[ \ln \left( \frac{z_{re} - d}{z_3 - d} \right) - \Psi_H \left( \frac{z_{re} - d}{L} \right) + \Psi_H \left( \frac{z_3 - d}{L} \right) \right]
\]  
(5)

where \(\kappa\) was the von-Kàrmàn constant (= 0.4), \(d\) the displacement height \((d = 0.75 \cdot h_c)\), \(\Psi_H\) the stability correction function for heat (Foken, 2008) and \(L\) the Obukhov length.

In the canopy, \(\tau_{tr}(L_i, i = 1,2)\) were derived from the vertical Tn profiles (Lehmann et al., 1999; Plake and Trebs, 2013):

\[
\tau_{tr}(L_i) = \ln \left[ \frac{C_{Tn_{z_l}}(L_i)}{C_{Tn_{z_u}}(L_i)} \right] / \lambda
\]  
(6)

where \(C_{Tn_{z_l}}\) and \(C_{Tn_{z_u}}\) were the measured Tn concentrations (in Bq m\(^{-3}\)) at the lower \((z_l)\) and upper \((z_u)\) heights of \(L_i\), and \(\lambda\) the radioactive decay rate \(\lambda = \ln 2 / T_{0.5} = 0.0125\) s\(^{-1}\) (Hànsel and Neumann, 1995).

3 Results

3.1 Meteorological conditions and mixing ratios

During the field experiment, low and high NO\(_x\) periods occurred that were directly coupled to the wind direction and could be attributed to two contrasting synoptic conditions characterized by different wind speeds (see Moravek et al., 2014b). Fig. 1a displays the dominance of south westerly winds at the site during 45% of the field experiment and their relation to relatively low NO\(_x\) levels (< 3 ppb). Contrastingly, winds from the north eastern sector were characterized by high NO\(_x\) levels often above 13 ppb (Fig. 1a). High NO\(_x\) episodes (up to 40 ppb) were accompanied with low wind speed (< 3 m s\(^{-1}\)) and low NO\(_x\) (< 5 ppb) with wind speeds greater than 3 m s\(^{-1}\) as shown in Fig. 1b. O\(_3\) levels exhibited the opposite dependency
The measured CO$_2$ levels generally showed a similar pattern for high and low NO$_x$ levels, while O$_3$ levels exhibited the opposite dependency on wind speed.

For further data analysis, defined criteria allowed to account for these specific relationships. In order to clearly separate entire days (24 h) of contrasting conditions from each other, the criteria were defined as low NO$_x$ or high NO$_x$ periods when (i) the mean daytime wind speed was $> 3$ m s$^{-1}$ and the wind direction mainly ranged between 180 and 270°, or (ii) the mean daytime wind speed was $< 3$ m s$^{-1}$ and the wind direction was mainly outside 180 – 270°, respectively. The wind direction definition was fulfilled during 96% of the low NO$_x$ periods and during 84% of the high NO$_x$ periods. Following these criteria, we identified eleven and nine days as low and high NO$_x$ periods, respectively, which were separately analyzed.

### 3.2 Vertical profiles of trace gases

Since the wind field drives of vertical exchange of scalars such as trace gases between vegetation and the atmosphere (Finnigan, 2000), it affects their vertical distribution. Passive tracers such as Rn and CO$_2$ are used especially at nighttime as indicators for vertical exchange processes within plant canopies (e.g., Trumbore et al., 1990; Nemitz et al., 2009). Generally, nighttime wind speed values of the low and high NO$_x$ periods were accordingly higher and lower, respectively. This was reflected by the in-canopy concentrations of both Rn and CO$_2$ (Fig. 2a–d). During nighttime when both gases are exclusively emitted by soil, a rather weak enrichment within the canopy (Fig. 2a,c) reflected higher wind speeds and thus enhanced exchange during the low NO$_x$ periods. In comparison, during the high NO$_x$ periods a strong in-canopy CO$_2$ and Rn accumulation was observed (Fig. 2b,d). During daytime, photosynthesis prohibits the use of CO$_2$ as passive tracer, whereas Rn profiles are
still useful as no biological processes such as stomatal uptake affect its concentration (Lehmann et al., 1999). The vertical exchange is generally enhanced during daytime causing dilution of the in-canopy Rn concentrations, which was especially pronounced during the low NO$_x$ periods (Fig. 2a) and was less evident during the high NO$_x$ periods (Fig. 2b), due to with generally lower wind speeds during the latter periods.

The vertical distribution of O$_3$ (Fig. 2e,f) reflected a typical pattern with lower mixing ratios closer to the ground and higher mixing ratios above. The diurnal O$_3$ maximum occurred during the afternoon around 16:00 CET (= UTC+1). Nevertheless, in the low NO$_x$ periods the diurnal O$_3$ maximum was much less pronounced compared to the high NO$_x$ periods with 35 ppb and 50 ppb, respectively. Furthermore, characteristic vertical O$_3$ distributions were observed during the low and high NO$_x$ periods. Nighttime O$_3$ gradients were less pronounced during the low NO$_x$ than during the high NO$_x$ periods. Median in-canopy values of O$_3$ were 10-20 ppb and were 20-25 ppb above the canopy during the low NO$_x$ periods (Fig. 2e). During the high NO$_x$ periods 1-6 ppb of O$_3$ were measured in the canopy and 10-25 ppb above the canopy (Fig. 2f).

During both the low and the high NO$_x$ periods, significantly enhanced NO mixing ratios prevailed during the morning hours from 06:00 to 14:00 CET (Fig. 2g,h) with median diurnal maxima of 0.6 ppb and 7.2 ppb, respectively, both occurring at 10:00 CET (not visible in Fig. 2h due to scaling). The NO mixing ratios decreased afterwards to approach nighttime minima. These were characterized by small vertical NO gradients during both periods. During low NO$_x$ nights, NO appeared to be mainly present in the in-canopy air layer, with median mixing ratios at $z_1$ and $z_2$ of $\leq 0.1$ ppb. The median values at $z_1$ and $z_2$ during the high NO$_x$ periods were $\leq 0.3$ ppb, respectively.
NO$_2$ mixing ratios were generally found to increase with height (Fig. 2i,j), featuring significantly stronger vertical differences during the high NO$_x$ periods. Similar to NO, also NO$_2$ mixing ratios were enhanced throughout the profile during the morning hours of both, low and high NO$_x$ periods, with corresponding values of 1–2.5 ppb and 6–14 ppb, respectively. At nighttime, comparable NO$_2$ mixing ratios of around 1 ppb prevailed during both periods at $z_1$. NO$_2$ showed stronger gradients above the canopy during the high NO$_x$ periods. The diurnal NO$_2$ minima during low and high NO$_x$ periods were observed between 12-16 CET and 14-16 CET, respectively.

3.3 Vertical profiles of chemical timescales

The obtained values for $\tau_{ch}$ were generally higher during nighttime than during daytime (Fig. 3a,d,g) and decreased/increased from $L_3$ to $L_1$. The validity of our applied criteria for separation between low and high NO$_x$ periods is shown by the median values (brown and green lines) that nearly adjoined the interquartile range of the overall data set. Significantly higher $\tau_{ch}$ values prevailed during nighttime of the high NO$_x$ periods, ranging from 300 to 2500 s in $L_{1-3}$. In contrast, low NO$_x$ periods were characterized by $\tau_{ch}$ of 250–800 s in $L_{1-3}$. However, during daytime $\tau_{ch}$ was within 100–200 s in $L_{1-3}$ for both periods. During the low NO$_x$ periods $\tau_{ch}$ values were slightly higher compared to the high NO$_x$ periods.

3.4 Vertical profiles of transport times

The median $\tau_{tr}(L_3)$ of all data Fig. 3b was one order of magnitude smaller during noon than at midnight with 30 and 200 s, respectively. As for $\tau_{ch}$ (Sect. 3.3), also in the case of $\tau_{tr}$ the medians of the low and high NO$_x$ periods adjoined the interquartile range of the overall data set. For example, $\tau_{tr}(L_3)$ in the low NO$_x$ periods never exceeded $\tau_{tr}(L_3)$ in the high NO$_x$ periods (cf. Fig. 3b). The difference of $\tau_{tr}(L_3)$ between noon and midnight was largest in the
high NO$_x$ and smallest during the low NO$_x$ periods with 470 s and 40 s, respectively. Compared to $L_{1-2}$ (Fig. 3e,h), the extreme values of the entire $\tau_{tr}$ data set were found above the canopy in $L_3$. The overall $\tau_{tr}$ minimum occurred during daytime of the low NO$_x$ periods, and the maximum during nighttime of the high NO$_x$ periods in $L_{3-4}$.

The diurnal course of $\tau_{tr}(L_2)$ from the entire data set in Fig. 3e exhibited a similar pattern as $\tau_{tr}(L_3)$, with higher $\tau_{tr}(L_2)$ during nighttime than during daytime. Representative nighttime and daytime values were 200 and 100 s, respectively, and a similar nighttime separation between the low and high NO$_x$ periods as in Fig. 3b was observed.

In contrast, both diurnal $\tau_{tr}(L_1)$ medians representing all data and the high NO$_x$ periods (Fig. 3h) were slightly higher during daytime between 08:00 and 13:00 CET than at nighttime with around 200 and 75–175 s, respectively. In the low NO$_x$ periods, the median $\tau_{tr}(L_1)$ was relatively constant throughout the day with about 200 s. The pattern of $\tau_{tr}(L_1)$ was generally opposite to $L_{2-3}$, with faster $\tau_{tr}(L_1)$ in the high NO$_x$ periods than in the low NO$_x$ periods.

### 3.5 Vertical profiles of Damköhler numbers

The values for $DA(L_3)$ presented in Fig. 3c were generally smaller during daytime than during nighttime. They exhibited a diurnal minimum of 0.2 and a maximum of 1.3 at 08:00 and 21:00 CET, respectively. In the low NO$_x$ periods, the difference of the $DA(L_3)$ median ($0.2 < DA(L_3) < 0.3$), to a $DA$ of unity was highest, whereas in the high NO$_x$ periods $DA(L_3)$ remained at higher median values ($0.3 < DA(L_3) < 3.9$).

In contrast, the diurnal course of $DA(L_2)$ in Fig. 3f exhibited its maximum of 1.25 at 15:00 CET and featured nighttime minima of about 0.3. The difference in $DA(L_2)$ between the low and high NO$_x$ periods was not as pronounced as for $DA(L_3)$. This became most
obvious from 15:00 to 24:00 CET with lower $DA(L_2)$ in the low NO$_x$ periods. Hence, both $DA(L_{2,3})$ values throughout the day were within or above the critical range for $DA$ or above under all conditions.

Interestingly, the diurnal course of $DA(L_1)$ (Fig. 3i) appeared nearly mirrored to $DA(L_3)$, with highest and lowest $DA$ during daytime and nighttime, respectively. The diurnal median of $DA(L_1)$ partly exhibited values below 0.1 (transport dominates) during nighttime of the high NO$_x$ periods, values above unity (chemistry dominates) from 12:00 to 17:00 CET under all conditions, and between 0.1 and unity during nighttime in the overall data set and in the low NO$_x$ periods.

4 Discussion

4.1 Transport times and resistances

4.1.1 Thermal stratification

The diurnal courses of the temperature differences $\Delta T(L_{1-3})$ in Fig. 4a–c describe the stability in each layer. They clearly indicated contrasting stability conditions in $L_1$ and $L_{2-3}$. During daytime, negative values of $\Delta T(L_{2-3})$ reflected unstable conditions, while positive $\Delta T(L_1)$ reflected stable conditions. In contrast, at nighttime these conditions were reversed. Similar diurnal cycles of stratifications are observed for other canopies (cf. Jacobs et al., 1994; Kruijt et al., 2000; Nemitz et al., 2000), and are known to decouple the lower canopy from the air layers above (cf. Fig. 4d). Canopy coupling regimes are typically classified according to the detection of coherent structures in high frequency time series of scalars such as temperature (e.g. Foken et al., 2012; Dupont and Patton, 2012). In our data set $\Delta T(L_1)$ could be used to explain why $\tau_{tr}(L_1)$ was generally smaller, i.e. transport was faster, during nighttime than...
during daytime (Fig. 3h). The soil released stored heat as thermal plumes during nighttime that drove an in-canopy nighttime convection, which reached up to the height of the temperature inversion as explained by Dupont and Patton (2012) or Jacobs et al. (1994). This effect caused the lower $\tau_{tr(L)}$ during nighttime. The $\tau_{tr(L)}$ maximum of 200 s from 08:00 to 13:00 CET could accordingly be attributed to positive $\Delta T(L)$ values at that time indicating a stable stratification. In all layers, the thermal stratification was stronger during the high NO$_x$ periods and weaker during the low NO$_x$ periods in all layers (Fig. 4a–c). This was caused by higher wind speeds during the low NO$_x$ periods causing increased turbulence and mixing that yielded smaller mixing and thus the vertical temperature differences were smaller.

### 4.1.2 Aerodynamic resistances and transport times

Aerodynamic resistances above ($R_a$) and within the canopy ($R_{ac}$) are important input parameters for modeling studies on surface-atmosphere exchange fluxes. They represent transport times through a layer, normalized by the layer thickness ($R_{a(c)} = \tau_{tr}/\Delta z$). In cases when the thicknesses of two layers under consideration differ, the effectiveness of transport can be represented by the corresponding aerodynamic resistances. On the other hand, transport times are required to evaluate the influence of chemical reactions on fluxes (e.g., $DA$).

Aerodynamic in-canopy resistances Typically, ($R_{ac}$) values are parameterized as function of $u^*$ and LAI (e.g., van Pul and Jacobs, 1994; Personne et al., 2009). These parameterizations are based on experiments above e.g., crops such as maize (van Pul and Jacobs, 1994) and consider a homogeneous vertically leaf distribution (Personne et al., 2009). However, this approximation may differ substantially within grassland canopies, as their structure is characterized by high biomass density in the lowest layer (cf. Sect. 2.1).
The usefulness importance of our results is underlined by the direct assessment of measured $R_{ac}$ values. From Eq. 6 we can assess $R_{ac}$ for different canopy layers ($L_1$, $L_2$ and for the whole canopy ($\tau_{tr}(z_1,z_3); \Delta z = z_3 - z_1$)) within the grassland canopy (cf. Fig. 5). In the lowermost canopy layer, $R_{ac}(L_1)$ was generally highest with medians of 900 to 1000 s m$^{-1}$ during nighttime and 1000 to 1300 s m$^{-1}$ during daytime (Fig. 5). In comparison, Gut et al. (2002) found the aerodynamic resistance in the lowest meter of an Amazonian rain forest canopy in a similar range and showing the same diurnal pattern with 600 s m$^{-1}$ during nighttime and 1700 s m$^{-1}$ during daytime, showing the same diurnal pattern.

As found for the transport times, the diurnal course of $R_{ac}$ was inversed in the upper layers above mirrored that of the lowermost layer (Fig. 5). In the upper canopy, the median of $R_{ac}(L_2)$ typically ranged around 300 s m$^{-1}$ during nighttime and around 150 s m$^{-1}$ during daytime. In comparison, above the canopy the median of $R_{ac}(L_3)$ (Eq. 5) was substantially lower with around 80 and 15 s m$^{-1}$ during nighttime and daytime, respectively. Consequently, the aerodynamic resistances in and above the canopy ($R_{ac}(L_{1,2})$ and $R_{ac}(L_3)$) differed by almost two orders of magnitude during daytime, and by one order of magnitude during nighttime.

Accordingly, the efficiency of aerodynamic transport decreased with decreasing height, even if the transport times were partly occasionally shorter in $L_1$ compared to $L_3$. The $R_{ac}$ for the entire canopy (Fig. 5) reflects the sum of the measured transport times divided by the entire layer thickness ($\Delta z = z_3 - z_1$) and can be considered as equivalent to a weighted average of $R_{ac}(L_1)$ and $R_{ac}(L_2)$ for the whole canopy (Fig. 5). $R_{ac}$ ranged in-between $R_{ac}(L_1)$ and $R_{ac}(L_2)$ with 440 s m$^{-1}$ during nighttime and 360 s m$^{-1}$ during daytime. The opposite diurnal courses of both, $R_{ac}(L_1)$ and $R_{ac}(L_2)$ have an impact on $R_{ac}$, which in turn showed a smaller diurnal variation. As $L_2$ contained around 80% of the layer thickness between $z_1$ and $z_3$ (cf. Fig. 5), $R_{ac}$ was closer to $R_{ac}(L_2)$. 
The median transport time through the 0.6 m high natural grassland canopy (also referred to as “canopy flushing time”) was presented in the related study of Plake and Trebs (2013) for the same experiment. It was measured using the vertical thoron profile between $z_1$ and $z_3$ (Eq. 6). The canopy flushing time is consistent with the sum of $\tau_{tr}(L_1)$ and $\tau_{tr}(L_2)$ in this manuscript (cf. Fig. 7 below) and represents the in-canopy layer down to $0.07 \cdot h_c (z_1/h_c)$. It was determined to be $\leq 6$ min exhibiting only small daytime/nighttime variation. Simon et al. (2005) reported canopy flushing times of around 60 min during any time of the day based on radon measurements within a 40 m high rain forest canopy. For the layer between $h_c$ and $0.13 \cdot h_c$ (canopy top to trunk space), they determined flushing times of around 60 min during any time of the day. As in the grassland canopy in Mainz-Finthen, nighttime in-canopy convection accounted for the small daytime/nighttime variation in their study. Normalization of their canopy flushing time by the layer thickness yielded $R_{ac}$ in the order of 100 s m$^{-1}$, which is around 3–4 times lower than the corresponding $R_{ac}$ of the grassland site. Other studies (Holzinger et al., 2005; Rummel, 2005) based on surface renewal models reported somewhat lower flushing times. Rummel (2005) found flushing times in a 32 m high rain forest canopy of $\leq 200$ s during daytime, which correspond to $R_{ac}$ values $\leq 10$ s m$^{-1}$. In the same way Holzinger et al. (2005) determined flushing times of 90 s during daytime and around 300 s during nighttime within a 6 m high scrubby pine forest. Corresponding $R_{ac}$ values were in the order of 20 and 60 s m$^{-1}$, respectively.

Thus, it is important to note that even if the canopy height of natural grassland canopies is small compared to forests (around 1–10 %); the corresponding canopy flushing times are of the same order of magnitude as those reported for forest canopies (10–400 %). The typically high biomass density in the lower canopy of grasslands (e.g., Jäggi et al., 2006; Nemitz et al., 2009) is the most obvious explanation. It provides a large aerodynamic re-
dynamic resistance is large enough to increase the overall aerodynamic resistance of the whole canopy \( R_{ac} \) by 50\% and 140\% during night and daytime, respectively. Consequently, \( R_{ac} \) of the grassland canopy was found at least 3–4 times higher than \( R_{ac} \) values representing corresponding in-canopy layers of forests taken from literature.

Plake and Trebs (2013) compared their directly measured transport times with the parameterizations of van Pul and Jacobs (1994) and Personne et al. (2009). They found that none of the parameterizations was able to reproduce the entire diurnal course of the in-canopy transport.

**4.2 Chemical timescales**

The non-linear profiles of NO, NO\(_2\) and O\(_3\) might have introduced uncertainties in \( \tau_{ch}(L_{1-3}) \).

The potential uncertainties due to averaging were investigated by determining the individual \( \tau_{ch}(z_{1-4}) \) and their subsequent comparison with \( \tau_{ch}(L_{1-3}) \). In \( L_1, L_2 \) and \( L_3 \) they were found to be \( \leq 13\% \), \( \leq 4\% \) and \( \leq 2\% \), respectively, during daytime under any condition. During nighttime, the uncertainties in \( L_2 \) and \( L_3 \) were found to be 6 and 2\% during the low NO\(_x\) periods and 57\% and 13\% during the high NO\(_x\) periods, respectively. In \( L_1 \) the uncertainty during nighttime was 30\% for all conditions. Furthermore, the in-canopy parameterization of \( j_{NO_2} \) might have introduced additional uncertainties since (i) in reality the attenuation of in-canopy radiation might be more complex than described in Eq. 3, and (ii) the parameterization of \( j_{NO_2} \) from \( G \) is prone to uncertainties of >40\% for \( G < 100 \text{ W m}^{-2} \), 10 – 40\% for \( G = 100–500 \text{ W m}^{-2} \) and \( \leq 10\% \) for \( G > 500 \text{ W m}^{-2} \) (Trebs et al., 2009). Moreover, omitting the influ-
ence of peroxy radical (HO₂+RO₂) levels for the calculation of the chemical timescales introduces uncertainties. However, measurements of vertical profiles of HO₂+RO₂ inside and above the grassland canopy are challenging and were not made during our experiment. Additionally, no straightforward analytical framework exists to calculate their influence on chemical timescales due to the variety of compounds and reaction rates involved in the complex HO₂/RO₂ chemistry, which would require numeral modelling (see Heal et al., 2001).

The diurnal maxima and minima of τ_{ch}(L_{1-3}) (Fig. 3a,d,g) were found to coincide with the O₃ minima and maxima (Fig. 2e,f), respectively. The impact of the terms in Eq. 2 on τ_{ch}(L₃) was examined by a correlation coefficient analysis. It was found to be highest for O₃ followed by NO₂ and NO with r = -0.57, r = 0.46 and r = -0.07, respectively. Consequently, the chemical timescale is dominated by the influence of O₃ as long as O₃ is present in excess compared to the other compounds. As the average air-chemical situation conditions in Mainz-Finthen, were characterized by a surplus of O₃ compared to NO₂ or NO (cf. Sect. 3.2), the magnitude of τ_{ch}(L₃) was most affected by the mixing ratios of O₃. In contrast, NO was generally less abundant, which explained the low overall impact on τ_{ch}(L₃). Only during high NO₃ situations, when NO levels were above 5 ppb (cf. Sect. 3.1), an increased impact of NO on τ_{ch}(L₃) was found.

Fig. 6a summarizes the chemical timescales. The temporal variation in τ_{ch}, expressed by higher nighttime and lower daytime values, can be considered as a rather typical pattern based on the diurnal courses of NO, NO₂ and O₃ (Fig. 2e–j) and their strong photochemical link. The vertical variation in τ_{ch}(L_{1-3}) was on the one hand caused by the attenuation of j_{NO₂} in the canopy, and on the other hand by generally increasing mixing ratios of NO, NO₂ and O₃ with height (Fig. 2e–j). It should be noted, that the latter finding was a site exclusively valid characteristic issue for this experimental site. Plake et al. (2014) measured insignificant soil
biogenic NO soil emissions were measured by Plake et al. (2014), and were underlined by weak in-canopy NO gradients (Fig. 2g,h). As already discussed in the previous paragraph, generally low NO, NO₂ and O₃ mixing ratios tend to cause high \( \tau_{ch} \) values and vice versa. Consequently, at a site with higher NO emissions as e.g., an intensively managed agricultural field, the vertical \( \tau_{ch} \) profile would most likely feature smaller vertical differences.

The extremely high \( \tau_{ch}(L_1) \) during nighttime of the high NOₓ periods (Fig. 6a) were a direct consequence of canopy decoupling (cf. Sect. 4.1.1). Transport of O₃ and NO₂ into the lower canopy was suppressed by the temperature inversion (cf. Fig. 2f,j). The residual O₃ and NO₂ molecules were convectively circulated within the lower canopy and, subsequently deposited efficiently to surfaces until both almost disappeared in the early morning (Fig. 2f,j). Thus, consequently, both the negligible NO emissions together with and the suppressed supply of O₃ and NO₂ from above, yielded simultaneously very low mixing ratios of all three trace gases, that in turn led to the extremely very high \( \tau_{ch}(L_1) \) values.

Our results are in line with those of Stella et al. (2013) who reported median diurnal \( \tau_{ch} \) of 80-300 s and 150-600 s above and within the canopy, respectively, for an intensively managed meadow. Their in-canopy \( \tau_{ch} \) maximum was somewhat lower than in Mainz-Finthen, which might be attributed to NO soil emissions or to averaging of different layers.

As mentioned above, the chemistry of HO₂/RO₂ is not considered in our study. The reaction rate constant of NO + HO₂/RO₂ is about 500 times higher than that of the reaction NO + O₃. Assuming relatively high average daytime HO₂ + RO₂ mixing ratios of 60 ppt inside the canopy (see Wolfe et al., 2014) the oxidation of NO to NO₂ would be as fast as with 30 ppb of O₃. This implies that these chemical timescales may be comparable to those of the reaction NO + O₃, which dominates \( \tau_{ch} \) derived from Eq. 2. However, it should be noted that peroxides have a high affinity to be lost at surfaces, which may reduce their presence in dense
grassland canopies. Since Eq. 2 exclusively considers R1 and R3, additional reactions may have biased the obtained $\tau_{ch}$ values to a certain extent. For instance, the oxidation of NO to NO$_2$ by peroxy radicals (Sect. 1). Additionally, or reactions between volatile organic compounds (VOCs) and O$_3$ (e.g., Atkinson and Arey, 2003) might have influenced ambient NO, NO$_2$ and O$_3$ levelschemical timescales. Simultaneously measured biogenic VOC mixing ratios featured very small values at our site (e.g., isoprene < 0.7 ppb, monoterpenes < 0.3 ppb, J. Kesselmeier, personal communication). Due to the absence of measurements the influence of anthropogenic VOCs is not taken into account. Thus, the latter reactions could be considered of minor importance, whereas information on peroxy radicals was unfortunately not available.

4.3 Influence of meteorology and air pollution on vertical Damköhler number profiles

The summarized daytime $DA(L_{1-3})$ in Fig. 6c exhibited a pattern of decreasing $DA$ values with increasing layer height. Thus, the likelihood of chemical flux divergence was indicated to decreased from $L_1$ to $L_3$. Throughout $L_1$ to $L_3$, the $\tau_{ch}$ values (Fig. 6a) showed a lower variation compared to the corresponding $\tau_{tr}$ values (Fig. 6b). Therefore, the daytime $DA$ profile was mainly caused by the vertical $\tau_{tr}$ profile.

Interestingly, the nighttime $DA$ of for all data and the high NO$_x$ periods showed opposite vertical profiles, indicating an increasing likelihood of chemical flux divergence with increasing layer height ($L_1$ to $L_3$). This was especially pronounced during nighttime of the high NO$_x$ periods, where the only instance without indication for a flux divergence within the entire data set for $L_1$ was found for $L_2$. The reasons for this were (i) the extraordinary very high $\tau_{ch}(L_1)$ (Fig. 6a and Sect. 4.2), and (ii) the reversed vertical transport time profiles during nighttime (fastest in $L_1$) of the high NO$_x$ periods (Fig. 6b). This finding agrees very well with
Rummel (2005) who found at nighttime that the transport timescale in the lowermost layer of an Amazonian rainforest to be faster than the chemical timescale of the NO-NO$_2$-O$_3$ triad during nighttime.

Above the canopy, the order of magnitude (Fig. 6c) and the median diurnal course (Fig. 3c) of $DA$ compared well with the values of Stella et al. (2013). But the in-canopy $DA$ of Stella et al. (2013) was smaller than the $DA$ above the canopy throughout the entire day, which is in contrast to our study. Considering the average canopy flushing time given in Plake and Trebs (2013) (cf. Sect. 4.1.2) and the $\tau_{ch}(L_2)$ (cf. Fig. 6a), a comparable average in-canopy $DA$ in Mainz-Finthen was in the order of 2 and 1 for daytime and nighttime, respectively. Thus, in our study in-canopy $DA$ in our study values are on average significantly higher than above the canopy throughout the day. As the canopy height in Stella et al. (2013) was only around 0.2 m, the corresponding transport time was faster with 80 s at noon which could explain the lower in-canopy $DA$ compared to our study. Finally, it should be noted that in-canopy $DA$ values within plant canopies may not be fully representative as are not fully representative for all processes, since besides transport and chemistry, additional sources and sinks for trace gases exist within plant canopies. These are specific for each trace gas and will be further discussed below.

4.4 Implications for measured fluxes

4.4.1 Potential NO$_x$ canopy reduction

Within the canopy, $DA(L_{1-2})$ (Fig. 3f,i; Fig. 6c) suggested that chemical reactions exhibited a larger influence on the NO-NO$_2$-O$_3$ triad during daytime than during night. However, reactive traces gases in canopies are deposited to soil and vegetation elements. Trace gases can be efficiently taken up by plants due to adsorption/absorption on cuticles and diffusion through
stomata (e.g., Breuninger et al., 2012). On the other hand, particularly NO is simultaneously produced by microbial processes and is subsequently released from soil. Although, the latter process could be neglected in this study due to insignificant NO soil emissions (Sect. 4.2), the uptake of NO\textsubscript{2} by plants, however, was investigated in order to draw general conclusions on potential NO\textsubscript{x} canopy reduction within natural grasslands canopies. Hence, additional information on the characteristic time scale of plant uptake ($\tau_u$) of NO\textsubscript{2} was required. Such time-scales $\tau_u(NO\textsubscript{2})$ integrated over the whole canopy ($L_{1+2}$) were estimated based on a resistance model (Baldocchi, 1988), following an approach of Rummel (2005) as:

$$\tau_u(x) = \left(\frac{1}{R_{Lx}} \cdot \frac{\Delta A}{\Delta z}\right)^{-1}$$  \hspace{1cm} (7)

where $x$ denoted the trace gas of interest (here $x = NO\textsubscript{2}$) and $R_{Lx}$ was the leaf resistance of $x$:

$$R_{Lx} = \left(\frac{1}{R_{blx} + R_{sx} + R_{mesx}} + \frac{2}{R_{blx} + R_{cutx}}\right)^{-1}$$  \hspace{1cm} (8)

with $R_{blx}$ being the leaf boundary layer resistance of $x$ calculated according to Personne et al. (2009), $R_{sx}$ the stomatal resistance of $x$ taken from Plake et al. (2014), $R_{mesx}$ the mesophyll resistance set to 200 s m\textsuperscript{-1} for NO\textsubscript{2} and $R_{cutx}$ the cuticular resistance set to 9999 s m\textsuperscript{-1} due to the unimportance of cuticular deposition for NO\textsubscript{2} (both values were taken from Stella et al. (2013)).

During daytime, the median of $\tau_u(NO\textsubscript{2})$ calculated from all data was typically found to be the shortest amongst all timescales relevant for NO\textsubscript{2} typically ranging between 90 and 160 s between 09:00 and 17:00 CET (Fig. 7). This timescale was closely followed by $\tau_{ch}(L_{1+2})$ exhibiting values between 100 and 200 s in the same time window period, but with a shorter lasting the minimum was slightly skewed towards the afternoon. In contrast, the values of $\tau_{tr}(L_{1+2})$, the canopy flushing time, $\tau_{tr}(L_{1+2})$, ranged from 250 to 290 s (Fig. 7) during this

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time. For a similar comparable natural grassland canopy with significant NO soil emissions, this would imply an efficient in-canopy conversion of NO to NO$_2$ during daytime, followed by an effective NO$_2$ plant uptake as the transport was found to be 2-3 times slower. Furthermore, the biomass density within the lowest 0.2 m of the canopy (i) strongly inhibits the transport, especially in $L_1$ during daytime (Fig. 5; Fig. 6b), and (ii) dampens attenuates the photolysis of NO$_2$ at the soil-canopy interface, the location where NO is usually emitted. This indicates that a strong potential for NO$_x$ canopy reduction occurring exists in such grassland ecosystems during daytime, if-in case the precondition of significant NO soil emissions is fulfilled. The presence of peroxy radicals may even amplify this process.

However, during nighttime, $\tau_u(NO_2)$ was found to be very large (Fig. 7) due to plant stomata closure. Hence, the role of turbulence-chemistry interactions ($DA(L_{1-2})$) was dominating over biological uptake processes. In $L_1$ the transport of soil emitted NO would be slowest under relatively windy nighttime situations (low NO$_x$ periods in Fig. 3h) due to undeveloped in-canopy convection. Thus, a considerably high mixing ratio of O$_3$ within the canopy (Fig. 2e) would lead to an efficient formation of NO$_2$ indicated by $DA(L_{1-2})$ close to unity. The uptake of NO$_2$ by plants would be insignificant (see above), and only soil deposition would lead to a small NO$_2$ depletion. Most likely, such nighttime conditions would lead to simultaneous NO$_2$ and NO canopy emission fluxes. During nights with low wind speeds (high NO$_x$ periods), the temperature inversion constitutes a “canopy lid”. Within the canopy ($L_{1+2}$) the reaction of residual O$_3$ (cf. Sect. 4.2) and soil emitted NO would compete with the O$_3$ deposition to surfaces. Subsequently, a mixture of NO and NO$_2$ would be trapped inside the canopy. Besides some minor in-canopy NO$_2$ losses (see above), a distinct NO and NO$_2$ release may occur in the morning hours, which has been observed for forests (cf. Foken et al., 2012; Dorsey et al., 2004; Jacob and Wofsy, 1990).
4.4.2 Influence on O₃ deposition flux

Similar to NOₓ, the application of in-canopy DA values for O₃ remains difficult, since plant uptake and deposition to plant surfaces and the soil are additional O₃ loss pathways besides chemistry. The characteristic timescale of O₃ plant uptake and soil deposition $\tau_u(O₃)$, shown in Fig. 7, was estimated using Eqs. 7 and 8, with $x = O₃$, $R_{mesx}$ set to 0 s m⁻¹ (Erisman et al., 1994) and $R_{cutx} = R_{nsx} - R_{soilx}$ (e.g., Lamaud et al., 2009). $R_{nsx}$ was taken from Plake et al. (2014) and $R_{soilx} = 240$ s m⁻¹ according to Lamaud et al. (2009). $\tau_u(O₃)$ ranged from 30 to 150 s, which clearly illustrates the dominance of in-canopy O₃ plant uptake and soil deposition. $\tau_u(O₃)$ was significantly faster than both $\tau_{tr}(L_{1-2})$ and $\tau_{ch}(L_{1-2})$ during the entire day (values are given in Sect. 4.4.1).

Consequently, only DA values above the canopy, i.e. $DA(L₃)$ in this study, are valid as an indicator for potential O₃ flux divergence. Because $DA(L₃)$ always exceeded 0.1 (Fig. 3c, Fig. 6c), a chemical flux divergence could not be excluded at the Mainz-Finthen site. Furthermore, $DA > 1$ (Fig. 3c) during the early evening hours clearly indicated potential flux divergence. During the low NOₓ periods, the probability for flux divergence was lowest. The influence of chemistry on O₃ deposition fluxes determined by Plake et al. (2014) at the Mainz-Finthen grassland site will be discussed below. The median O₃ fluxes for the entire measurement period ranged from about -1.5 to -6 nmol m⁻² s⁻¹ during night and daytime, respectively. Due to negligible NO soil emissions, a chemical flux divergence in $L₃$ resulting from counter-directed fluxes of NO and O₃ was very unlikely. Nevertheless, we used a simplified method proposed by Duyzer et al. (1995) based on R1 and R3 and the law of mass conservation to approximate the flux divergence is approximated by the correction factor $\alpha_{O₃}$ as:
\[ \alpha_{O_3} = \frac{\phi_x}{k_{u_*}} \cdot \left[ k_1 \cdot \left( N_{NO} \cdot F_{O_3}^* + N_{O_3} \cdot F_{NO}^* \right) - j_{NO_2} \cdot F_{NO_2}^* \right] \]  

(9)

where \( \phi_x = \phi_{O_3} = \phi_H \) was the stability correction function for heat (Högström, 1988), \( F_{O_3}^* \)
the measured O\(_3\) flux at \( z_{ref} \) determined by the eddy covariance method (cf. Plake et al., 2014) and \( F_{NO}^* \) and \( F_{NO_2}^* \) the corresponding NO and NO\(_2\) fluxes determined by the dynamic chamber technique (cf. Plake et al., 2014). The estimated O\(_3\) deposition flux at \( z_3 \) (\( F_{z_3} \)) was then calculated as:

\[ F_{z_3} = F_{z_{ref}} + \int_{z_3}^{z_{ref}} \left( \frac{\partial F}{\partial z} \right)_z \, dz = F_{O_3}^* + \alpha_{O_3} \cdot z_3 \cdot \left( 1 + \ln \frac{z_{ref}}{z_3} \right) \]  

(10)

where the term \( \int_{z_3}^{z_{ref}} \left( \frac{\partial F}{\partial z} \right)_z \, dz \) was the integrated flux divergence within \( L_3 \). The resulting median O\(_3\) flux divergence was quantified to be less than 1 \%, confirming the our a priori assumption of irrelevant O\(_3\) flux divergence.

Nevertheless, we examined the influence of the enhanced NO mixing ratios in the morning hours (Sect. 3.2, Fig. 2g,h), accompanied by very low O\(_3\)/NO ratios (Fig. 8) on the measured O\(_3\) fluxes. A chemically induced O\(_3\) flux \( F_c(O_3) \) due to production \( P(O_3) \) or loss \( L(O_3) \) of O\(_3\) by R1 and R3 integrated over the air column of \( L_3 \) was quantified according to Rummel et al. (2007) as:

\[ F_c(O_3) = P(O_3) - L(O_3) = \int_{z_3}^{z_{ref}} \frac{\mu_{NO_2}(x) \cdot \rho_d(x)}{\tau_{NO_2}(x)} \cdot dz - \int_{z_3}^{z_{ref}} \frac{\mu_{O_3}(x) \cdot \rho_d(x)}{\tau_{O_3}(x)} \cdot dz \]  

(11)

where \( \rho_d \) (in mol m\(^{-3}\)) was the molar density of dry air. \( \tau_{NO_2} \) and \( \tau_{O_3} \) (in s) were the chemical depletion times of NO\(_2\) and O\(_3\), respectively:

\[ \tau_{NO_2} = \frac{1}{j_{NO_2}} \]  

(12)

\[ \tau_{O_3} = \frac{1}{k_1 N_{NO}} \]  

(13)
Fig. 9a displays the diurnal courses of $P(O_3)$ and $L(O_3)$ exhibiting median values of 0 to 1.9 nmol m$^{-2}$ s$^{-1}$ and 0 to -1.4 nmol m$^{-2}$ s$^{-1}$, respectively. The maximum median values were related to the enhanced NO$_x$ levels in the morning. The resulting median net $F_c(O_3)$ in Fig. 9b ranged between 0.6 and -0.05 nmol m$^{-2}$ s$^{-1}$, representing a net O$_3$ production in daytime and a net loss during nighttime. Repeatedly, the medians of low and high NO$_x$ periods adjoined the interquartile range of the overall data set, showing a variability of one order of magnitude of net $F_c(O_3)$ during daytime. Considering the median values of all data, the measured chemical contribution to the measured EC flux of O$_3$ deposition flux would be change by around +10% during daytime and -3% during nighttime. Consequently, the actual daytime O$_3$ deposition to the canopy is higher than measured by the EC method. This finding is interesting, as to our knowledge previous studies only reported chemical O$_3$ losses above the canopy when dealing with the chemical flux divergence of O$_3$. The due to outbalancing of the reactions of O$_3$ with NO (e.g., Dorsey et al., 2004) or VOCs (e.g., Kurpius and Goldstein, 2003) emitted by soil or plants, respectively, resulted in net O$_3$ loss. The net O$_3$ production in our study was attributed to a deviation from the NO-NO$_2$-O$_3$ photostationary state by a surplus of NO$_2$, based on NO oxidation by e.g. peroxy radicals or other oxidants (cf. Trebs et al., 2012). Unfortunately, we were not able to assess the impact of these reactions involved in the net O$_3$ production on the calculated chemical timescales as measurements of peroxy radicals were not available. The NO$_2$ surplus might have originated from simultaneous emissions of non-methane hydrocarbons, carbon monoxide (CO) and NO from motorways surrounding the site in a distance of some kilometers. It is well known that under daytime conditions peroxy radicals are formed that can oxidize NO without consumption of O$_3$ resulting in net O$_3$ production (Seinfeld and Pandis, 2006). Although, this O$_3$ production might also prevail at other experimental sites, this effect is most likely balanced or even exceeded by the
destruction of O$_3$ due to biogenic soil NO emissions which were negligible at our site (a nutrient poor grassland site).

5 Conclusions

For the first time, we simultaneously measured transport times (aerodynamic resistances), vertical profiles of NO-NO$_2$-O$_3$ mixing ratios and micrometeorological quantities within and above a natural grassland canopy. The obtained data were analyzed to gain insights about the potential NO$_x$ canopy reduction in the grassland canopy, and to analyze the effect contribution of chemistry on fluxes of purely depositing compounds, such as O$_3$. We observed two extreme regimes: a) the first characterized by high wind speed and low NO$_x$ mixing ratios (low NO$_x$ periods) and b) the second by low wind speed and high NO$_x$ mixing ratios (high NO$_x$ periods). Our study highlights that (i) as a result of in-canopy convection, nighttime transport in the lowest lowermost canopy layer is fastest, while during highly stable conditions above the canopy are highly stable due to low wind speed (during the high NO$_x$ periods).

Interestingly, our results on transport-chemistry interactions within the grassland canopy are partly comparable to those found in the Amazonian rainforest, although the vertical canopy structure differs substantially. Natural grasslands exhibit very high biomass densities in the lowest canopy part. Thus, the median aerodynamic resistance in the lowest canopy layer (0.04–0.2 m) was found to be of the same magnitude (> 900 s m$^{-1}$) and to feature the same diurnal pattern (higher during daytime, lower at night) as the aerodynamic resistance determined for the lowest meter of an Amazonian rain forest. The median in-canopy aerodynamic resistance representing the whole grassland canopy was at least 3–4 times higher than in-canopy aerodynamic resistances of forest canopies available from literature. Our results reveal that even if the canopy height of natural grassland canopies is small compared to for-
ests (around 1–10 %), the corresponding canopy flushing times are of the same order of magnitude as those reported for forest canopies (10–400 %). The median canopy flushing times exhibited only small daytime/nighttime variability, which is well in accordance with a detailed study on flushing times within an Amazonian rain forest (Simon et al., 2005). The small daytime/nighttime variability is caused by the compensating transport efficiencies in the lower and upper canopy layers during daytime and nighttime for both canopy types. The median canopy flushing time of the grassland was found to be \( \leq 6 \) min and the chemical timescale of the NO-NO\(_2\)-O\(_3\) triad during daytime ranged between 1–3 min. This has obvious implications e.g., for soil emitted reactive compounds such as NO, potentially implying fast chemical conversion of NO to NO\(_2\) within the grassland canopy. During daytime the plant uptake of NO\(_2\) was shown to be 2–3 times faster than the canopy flushing time. Inevitably, this leads to a strong potential NO\(_x\) canopy reduction in the presence of biogenic NO soil emissions. This effect may be amplified in case substantial levels of peroxy radicals prevail inside the canopy. Due to the extensive global terrestrial coverage with grassland canopies, this finding is highly relevant for the application of global chemistry and transport models.

Our results clearly indicate that the daytime NO\(_x\) canopy reduction for grasslands to may be much higher than 64 %. Nevertheless, an improved daily averaged for the NO\(_x\) canopy reduction factor in analogy to the one in Yienger and Levy (1995) cannot be presented here due to the insignificant NO soil emissions at the experimental site. Moreover, we determined a median net chemical O\(_3\) production of 10 % during daytime within the air column between the EC flux measurement and the canopy, which was due to the absence of soil biogenic NO soil emission in our study. Hence, in contrast to previous studies our measured O\(_3\) deposition flux by eddy covariance EC is slightly underestimated. The chemical flux divergence for O\(_3\) was one order of magnitude larger during the high NO\(_x\)
than during the low NO\textsubscript{x} periods. In-canopy Damköhler numbers were shown to be relevant for NO\textsubscript{2} only under nighttime conditions, which was due to the minor role of NO\textsubscript{2} uptake by plants at this time. Above the canopy Damköhler numbers above the canopy indicated a potential flux divergence, but did not provide a hint for the observed chemical production of O\textsubscript{3}. The only instance without indication for a chemical flux divergence within the entire data set was found during nighttime of the high NO\textsubscript{x} periods in the lowest lowermost canopy layer.

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Figures

Fig. 1. (a) Frequency distribution of wind direction related to NO\textsubscript{x} mixing ratios; (b) NO\textsubscript{x} mixing ratios as function of wind speed (ws) at the Mainz-Finthen grassland site.
Fig. 2. Time height cross sections indicating the median vertical distribution of (a,b) Rn, (c,d) CO$_2$, (e,f) O$_3$, (g,h) NO and (i,j) NO$_2$ during low NO$_x$ (left panels) and high NO$_x$ (right panels) conditions at the Mainz-Finthen grassland site. The canopy height (dotted line) and $L_{1-3}$ are also shown. The plots were made using the contourf function of MATLAB.
Fig. 3. Diurnal courses of (a, d, g) $\tau_{ch}(L_{1-3})$, (b, e, h) $\tau_{rr}(L_{1-3})$ and (c, f, i) $DA(L_{1-3})$ considering all data from 19 August to 26 September 2011 (medians and shaded interquartile ranges) and the low NO$_x$ and high NO$_x$ periods (green and brown medians and interquartile boxes) at the Mainz-Finthen grassland site.
Fig. 4. (a)–(c) Diurnal courses of measured $\Delta T(L_{1-3})$ considering all data from 19 August to 26 September 2011 (medians and shaded interquartile ranges) and the low and high NO$_x$ periods (green and brown medians and interquartile ranges); note: $\Delta T(L_1, L_3)$ do not fully cover $L_1$ and $L_3$ (Sect. 2.3) due to availability of measurements (Sect. 2.2); (a) $\Delta T(L_3)$: 2.5 – 0.8 m; (b) $\Delta T(L_2)$: 0.8 – 0.2 m; (c) $\Delta T(L_1)$: 0.2 – -0.02 m (soil temperature). (d) Median vertical temperature profiles and interquartile boxes representing the thermal stratification at 00:00 and 12:00 CET considering all data from 19 August to 26 September 2011 at the Mainz-Finthen grassland site.
Fig. 5. Diurnal courses of in-canopy aerodynamic resistances for each individual canopy layer ($R_{ac}(L_1)$, $R_{ac}(L_2)$) and for the entire grassland canopy ($R_{ac} = \frac{\tau_{er}(L_1) + \tau_{er}(L_2)}{z_3 - z_1}$) at the Mainz-Finthen site (median and shaded interquartile ranges). For comparison, the aerodynamic resistance above the canopy is also displayed ($R_a(L_3)$). The layer thickness ($\Delta z$) is indicated. The plots include all data from 19 August until 26 September 2011.
Fig. 6. Comparison of box plot statistics for $\tau_{ch}(L_{1-3})$, $\tau_{tr}(L_{1-3})$ and $DA(L_{1-3})$ during daytime and nighttime including all data from 19 August until 26 September 2011 separated for the low and high NO$_x$ periods at the Mainz-Finthen grassland site.

Fig. 7. Comparison of median diurnal $\tau_u(NO_2)$, $\tau_u(O_3)$, $\tau_{tr}$ and $\tau_{ch}$ with interquartile ranges for the whole canopy layer ($L_{1+2}$) considering all data from 19 August to 26 September 2011 at the Mainz-Finthen grassland site.
Fig. 8. Diurnal course of the O₃ to NO ratio in L₃ considering all data from 19 August to 26 September 2011 (median and shaded interquartile range) and separated for the low NOₓ and high NOₓ periods (medians and interquartile boxes) at the Mainz-Finthen grassland site.
Fig. 9. Diurnal courses showing (a) $P(O_3)$ and $L(O_3)$ and (b) $F_c(O_3)$ (Eq. 11) for $L_3$ considering all days from 19 August to 26 September 2011 (medians and shaded interquartile ranges) and separated for the low and high $NO_x$ periods (medians) at the Mainz-Finthen grassland site.