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 ~~part~~. 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 (NO_2) and ozone (O_3).

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 NO_x ($NO+NO_2$) 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}, ~~thus~~ which is as high as values ~~from literature representing~~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) suggest~~ed~~ a strong flux divergence for the NO-NO_2-O_3 triad within the canopy during daytime. ~~At~~ During that time, the timescale of NO_2 ~~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 O_3. 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 NO_2 by ~~the~~ plants. Furthermore, ~~a~~ photo-chemical O_3 production was observed above the canopy ~~was observed~~, which was attributed to a deviation from the NO-NO_2-O_3 photostationary state by a surplus of NO_2 due to oxidation of NO by e.g., peroxy radicals. ~~which resulted from a surplus of NO_2 from the NO-NO_2-O_3 photostationary state~~. The O_3 production was one order of magnitude higher during high NO_x than during low NO_x periods and resulted in an underestimation of the O_3 deposition flux measured with the EC method ~~underestimation, which was observed for the first time~~.

1 Introduction

Nitric oxide (NO) and nitrogen dioxide (NO_2) play a crucial role in air chemistry ~~since~~ as they act as key catalysts for ozone (O_3) production and are therefore involved in the generation of hydroxyl radicals (OH) (Crutzen, 1973). The most significant tropospheric source of O_3 is initiated by photochemical dissociation of NO_2 and subsequent reaction of the oxygen (O) atom with molecular oxygen:

$$NO_2 + h\nu\ (\lambda < 420\ \mathrm{nm}) \rightarrow NO + O(^3P) \qquad \text{(R1)}$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \qquad \text{(R2)}$$

~~When~~ In case O_3 is present, it may oxidize NO and re-form NO_2:

$$O_3 + NO \xrightarrow{k_3} NO_2 + O_2 \qquad \text{(R3)}$$

In the absence of additional reactions, R1–R3 represent a null cycle. Besides R1–R3, NO is oxidized by peroxy radicals (HO_2+RO_2), which ~~onstituting~~ constitutes an ~~additional~~ important net O_3 production pathway in the troposphere (Warneck, 2000).

Dry deposition to terrestrial surfaces, especially to plant canopies, is an important sink for tropospheric O_3 and NO_2. The uncertainties of dry deposition estimates are substantially higher for NO_2, because its net ecosystem exchange can be bi-directional depending on the ambient NO_2 levels (Lerdau et al., 2000). O_3 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 NO_x ($NO+NO_2$) emissions (~~IPPC, 2007~~IPPC, 2013), highlighting the need of ~~careful~~ detailed investigations on NO_x 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_2 originating from biogenic soil NO emissions after reaction with O_3 within plant canopies (Rummel et al., 2002) is accounted for in global models by a so-called canopy reduction factor for NO_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, t~~The contrasting canopy structure of grassland and forest ecosystems highlights the need for a detailed analysis and an evaluation of the suggested NO_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_{tr}) and the characteristic chemical timescale (τ_{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., 2014a). 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 ~~was~~ is ~~situated~~ located 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, Ansyco 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, ~~is focused~~ focuses on the period from 19 August to 26 September 2011 ~~were~~ 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, ~~Glashütten~~Königstein, 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 m), L_2 the upper canopy layer between z_{2-3} ($\Delta z(L_2)$ = 0.6 m), and L_3 the layer above the canopy between z_3 and z_{ref} ($\Delta z(L_3)$ = 2.2 m). As shown in Plake et al. (2014) the vertical trace gas gradients between z_{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 τ_{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:

$$\tau_{ch}(L_i) = \frac{2}{\sqrt{j_{NO_2}(L_i)^2 \cancel{j_{NO_2}(L_i)} + k_3(L_i)^2 \cancel{k_1(L_i)} \cdot (N_{O_3}(L_i) \cancel{+} - N_{NO}(L_i))^2 + 2 j_{NO_2}(L_i) \cdot k_3(L_i) \cdot (N_{O_3}(L_i) + N_{NO}(L_i) + 2N_{NO_2}(L_i))^{\cancel{2}}}} \quad (2)$$

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 O_3, NO or NO_2 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. RO_2 +NO) are not included.
- covariance terms and other budget terms i.e. horizontal and vertical advection, flux divergence and change in O_3 mixing ratio d[O_3]/dt are neglected.

2.3.2 NO_2 photolysis 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):

$$G(LAI) = G_0 \cdot \exp^{(-k_{ex} \cdot LAI)} \tag{3}$$

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):

$$\tau_{tr}(L_3) = R_a(L_3) \cdot \Delta z(L_3) \tag{4}$$

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

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

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

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

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 λ the radioactive decay rate $\lambda = \ln 2 / T_{0.5} = 0.0125$ s^{-1} (Hänsel 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~~ above 3 m s^{-1} as shown in Fig. 1b. O_3 levels exhibited the opposite dependency

on wind speed, while ~~T~~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 *ws*~~.

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 ~~*ws*~~ was > 3 m s^{-1} and the wind direction mainly ranged between 180 and 270°, or (ii) the mean daytime wind speed ~~*ws*~~ 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 NOx periods. Following these criteria, we identified eleven and nine days as low and high NO_x periods, respectively, which were ~~separately~~ analyzed separately.

3.2 Vertical profiles of trace gases

Since the wind field ~~is the driver~~ 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 ~~*ws* values~~ wind speeds during~~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 ~~*ws*~~ 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 ~~in~~ 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 ~~10-25 ppb~~ (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 ≤ 0.1 ppb. The median values at z_1 and z_2 during the high NO_x periods were ≤ 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 τ_{ch} were generally higher during nighttime than during daytime (Fig. 3a,d,g) and ~~decrease~~ 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 adjoin~~ed~~ the interquartile range of the overall data set. Significantly higher τ_{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 τ_{ch} of 250–800 s in L_{1-3}. However, during daytime τ_{ch} was within 100–200 s in L_{1-3} for both periods. During the low NO_x periods τ_{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 τ_{ch} (Sect. 3.3), also in the case of τ_{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 τ_{tr} data set were found above the canopy in L_3. The overall τ_{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~~L_3~~.

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~~ is 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~~ During 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~~ During 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~~It~~ ~~became~~ was 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 that of ~~inverted 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 indicate~~d~~ 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~~was 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~~ found by Dupont and Patton (2012) or Jacobs et al. (1994). ~~This effect caused the lower $\tau_{tr}(L_1)$ during nighttime.~~ The $\tau_{tr}(L_1)$ maximum of 200 s from 08:00 to 13:00 CET could accordingly be~~en~~ attributed to positive $\Delta T(L_1)$ values at that time indicating a stable stratification. ~~In all layers~~ T~~t~~he 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 ~~that yielded better 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~~ are considered as important input ~~parameters~~ variables for modeling studies on surface-atmosphere exchange fluxes. They ~~represent~~ can be derived from the 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 ~~typically~~ 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~~ of 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 $R_a(L_3)$ (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 $R_a(L_3)$) 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 ≤ 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~~ 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 ≤ 200 s during daytime, which correspond to R_{ac} values ≤ 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~~are within 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-

sistance (> 900 s m^{-1}) in a small layer adjacent to the ground (here: $R_{ac}(L_1)$). ~~The~~ This ~~aerodynamic~~ 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. ~~An a~~Agreement with the measured transport times was either found during daytime (Personne et al., 2009) or nighttime (van Pul and Jacobs, 1994), underlining the need for more direct measurements on 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 ≤ 13 %, ≤ 4 % and ≤ 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 W m^{-2}, 10 – 40 % for G = 100–500 W m^{-2} and ≤ 10% for G > 500 W m^{-2} (Trebs et al., 2009). Moreover, omitting the influ-

ence of peroxy radical (HO_2+RO_2) levels for the calculation of the chemical timescales introduces uncertainties. However, measurements of vertical profiles of HO_2 + RO_2 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 HO_2/RO_2 chemistry, which would require numeral modelling (see Heal et al., 2001).

The diurnal maxima and minima of $\tau_{ch}(L_{1-3})$ (Fig. 3a,d,g) were found to coincide with the O_3 minima and maxima (Fig. 2e,f), respectively. The impact of the terms in Eq. 2 on $\tau_{ch}(L_3)$ was examined by a correlation coefficient analysis. It was found to be highest for O_3 followed by NO_2 and NO with r = -0.57, r = 0.46 and r = -0.07, respectively. Consequently, the chemical timescale is dominated by the influence of O_3 as long as O_3 is present in excess compared to the other compounds. As the average air-chemical ~~situation~~ conditions in Mainz-Finthen~~,~~ ~~was~~ were characterized by a surplus of O_3 compared to NO_2 or NO (cf. Sect. 3.2), the magnitude of $\tau_{ch}(L_3)$ was most affected by the mixing ratios of O_3. In contrast, NO was generally less abundant, which explained the low overall impact on $\tau_{ch}(L_3)$. Only ~~under~~ during high NO_x ~~situations~~periods, when NO levels were above 5 ppb (cf. Sect. 3.1), an increased impact of NO on $\tau_{ch}(L_3)$ 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, NO_2 and O_3 (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_{NO_2} in the canopy, and on the other hand by generally increasing mixing ratios of NO, NO_2 and O_3 with height (Fig. 2e–j). It should be noted, that the latter finding ~~was~~ is ~~a site~~exclusively valid ~~characteristic issue~~for this experimental site. Plake et al. (2014) measured ~~I~~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, NO_2 and O_3 mixing ratios tend to cause high τ_{ch} ~~-~~values and vice versa. Consequently, at a site with higher NO emissions as e.g., an intensively managed agricultural field, the vertical τ_{ch} profile would most likely feature smaller vertical differences.

The extremely high $\tau_{ch}(L_{1,})$ during nighttime of the high NO_x periods (Fig. 6a) were a direct consequence of canopy decoupling (cf. Sect. 4.1.1). Transport of O_3 and NO_2 into the lower canopy was suppressed by the temperature inversion (cf. Fig. 2f,j). The residual O_3 and NO_2 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 O_3 and NO_2 from above~~,~~ yielded ~~simultaneously~~ very low mixing ratios of all three ~~species~~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 τ_{ch} of 80-300 s and 150-600 s above and within the canopy, respectively, for an intensively managed meadow. Their in-canopy τ_{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 HO_2/RO_2 is not considered in our study. The reaction rate constant of NO + HO_2/RO_2 is about 500 times higher than that of the reaction NO + O_3. Assuming relatively high average daytime HO_2 + RO_2 mixing ratios of 60 ppt inside the canopy (see Wolfe et al., 2014) the oxidation of NO to NO_2 would be as fast as with 30 ppb of O_3. This implies that these chemical timescales may be comparable to those of the reaction NO + O_3, which dominates τ_{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 τ_{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 levels~~chemical timescales. Simultaneously measured biogenic VOC mixing ratios featured very small values at our site (e.g., isoprene < 0.7 ppb, monoterpene < 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 τ_{ch} values (Fig. 6a) showed a lower variation compared to the corresponding τ_{tr} values (Fig. 6b). ~~Therefore~~Hence, the daytime DA profile was mainly caused by the vertical τ_{tr} profile.

Interestingly, the nighttime DA ~~of~~ for all data and the high NO_x periods ~~data~~ 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_1~~. 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 ~~lowest~~ lowermost layer of an Amazonian rainforest ~~to be~~is 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 t~~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~~ the 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) suggest~~ed~~ 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_2 by plants, however, was investigated in order to draw ~~general~~ conclusions on potential NO_x canopy reduction within natural grasslands canopies. Hence, ~~additional information on~~ the characteristic time scale of plant uptake (τ_u) of NO_2 ~~was required. Such timescales $\tau_u(NO_2)$~~ integrated over the whole canopy (L_{1+2}) ~~were~~ was estimated based on a resistance model (Baldocchi, 1988), following an approach of Rummel (2005) as:

$$\tau_u(x) = \left(\frac{1}{R_{L_x}} \cdot \frac{\Delta LAI}{\Delta z}\right)^{-1} \tag{7}$$

where x denoted the trace gas of interest (here x = NO_2) and R_{L_x} was the leaf resistance of x:

$$R_{L_x} = \left(\frac{1}{R_{bl_x}+R_{s_x}+R_{mes_x}} + \frac{2}{R_{bl_x}+R_{cut_x}}\right)^{-1} \tag{8}$$

with R_{bl_x} being the leaf boundary layer resistance of x calculated according to Personne et al. (2009), R_{s_x} the stomatal resistance of x taken from Plake et al. (2014), R_{mes_x} the mesophyll resistance set to 200 s m^{-1} for NO_2 and R_{cut_x} the cuticular resistance set to 9999 s m^{-1} due to the unimportance of cuticular deposition for NO_2 (both values were taken from Stella et al. (2013)).

During daytime, the median of $\tau_u(NO_2)$ calculated from all data was typically found to be the shortest amongst all timescales relevant for NO_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

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~~,~~. H~~h~~ence, 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 ~~ws~~ 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 ~~deposition~~. 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 O_3 deposition flux

Similar to NO_2, the application of in-canopy DA values for O_3 remains difficult, since plant uptake and deposition to plant surfaces and the soil are additional O_3 loss pathways~~ besides chemistry~~. The characteristic timescale of O_3 plant uptake and soil deposition $\tau_u(O_3)$, shown in Fig. 7, was estimated using Eqs. 7 and 8, with x = O_3, R_{mes_x} set to 0 s m^{-1} (Erisman et al., 1994) and $R_{cut_x} = R_{ns_x} - R_{soil_x}$ (e.g., Lamaud et al., 2009). R_{ns_x} was taken from Plake et al. (2014) and R_{soil_x} = 240 s m^{-1} according to Lamaud et al. (2009). $\tau_u(O_3)$ ranged from 30 to 150 s, which clearly illustrates the dominance of in-canopy O_3 plant uptake and soil deposition. $\tau_u(O_3)$ 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. $DA(L_3)$~~ in this study~~, ~~are valid as an~~provides an ~~indicator~~ indication for potential O_3 flux divergence. ~~Because~~ Since the $DA(L_3)$ 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~~the dominance of chemical reactions over transport. During~~In~~ the low NO_x periods, the probability for~~of~~ flux divergence was lowest. The influence of chemistry on O_3 deposition fluxes determined by Plake et al. (2014) at the Mainz-Finthen grassland site will be discussed below. The median O_3 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 L_3 resulting from counter-directed fluxes of NO and O_3 was very unlikely. Nevertheless, we use~~d~~ a simplified method proposed by Duyzer et al. (1995) based on R1 and R3 and the law of mass conservation to approximate~~. T~~ the flux divergence ~~is approximated~~ by the correction factor α_{O_3} as:

$$\alpha_{O_3} = \frac{\phi_x}{\kappa \cdot u_*} \cdot \left[k_1 \cdot \left(N_{NO} \cdot F^*_{O_3} + N_{O_3} \cdot F^*_{NO}\right) - j_{NO_2} \cdot F^*_{NO_2}\right] \quad (9)$$

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:

$$F_{z_3} = F_{z_{\mathrm{ref}}} + \int_{z_3}^{z_{ref}} \left(\frac{\partial F}{\partial z}\right)_z dz = F^*_{O_3} + \alpha_{O_3} \cdot z_3 \cdot \left(1 + \ln \frac{z_{ref}}{z_3}\right) \quad (10)$$

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:

$$F_c(O_3) = P(O_3) - L(O_3) = \int_{z_3}^{z_{ref}} \frac{\mu_{NO_2}(z) \cdot \rho_d(z)}{\tau_{NO_2}(z)} \cdot dz - \int_{z_3}^{z_{ref}} \frac{\mu_{O_3}(z) \cdot \rho_d(z)}{\tau_{O_3}(z)} \cdot dz \quad (11)$$

where ρ_d (in mol m^{-3}) was the molar density of dry air. τ_{NO_2} and τ_{O_3} (in s) were the chemical depletion times of NO_2 and O_3, respectively:

$$\tau_{NO_2} = \frac{1}{j_{NO_2}} \quad (12)$$

$$\tau_{O_3} = \frac{1}{k_1 \cdot N_{NO}} \quad (13)$$

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~~ maximal 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 L_3 during 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 the~~se~~ 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 ~~related~~ 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 ~~in~~ 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~~ 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 ≤ 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 reveal~~indicate that the daytime NO_x canopy reduction for grasslands ~~to~~ may be ~~be much~~ higher than 64 %. Nevertheless, an improved daily average~~d~~ 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, ~~W~~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_x periods. In-canopy Damköhler numbers were shown to be relevant for NO_2 only under nighttime conditions, which was due to the minor role of NO_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_3. The only instance without indication for a chemical flux divergence within the entire data set was found during nighttime of the high NO_x periods in the ~~lowest~~ lowermost canopy layer.

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Figures

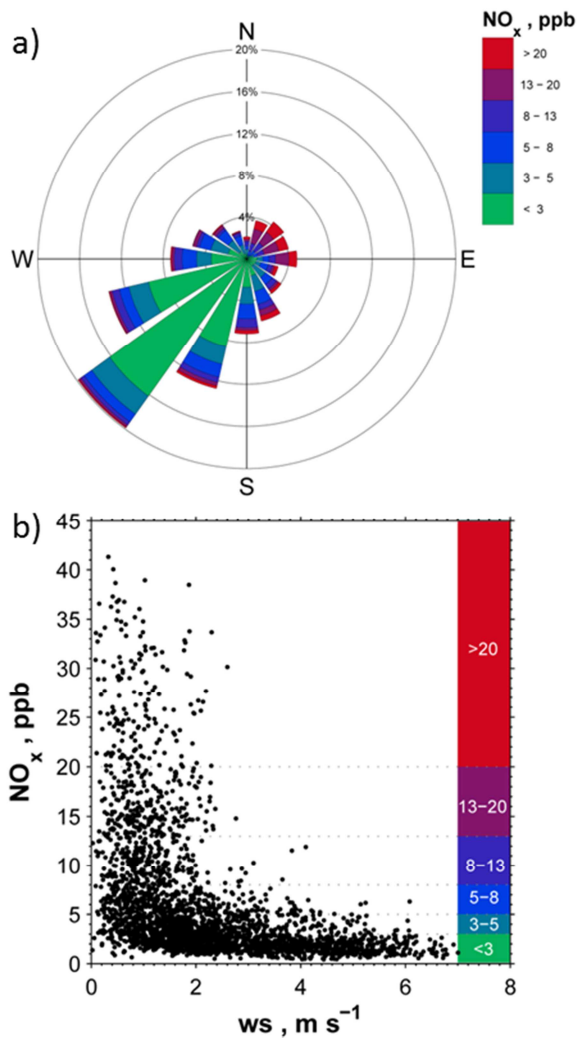

Fig. 1. (a) Frequency distribution of wind direction related to NO_x mixing ratios; (b) NO_x mixing ratios as function of ~~*ws*~~ wind speed (ws) at the Mainz-Finthen grassland site.

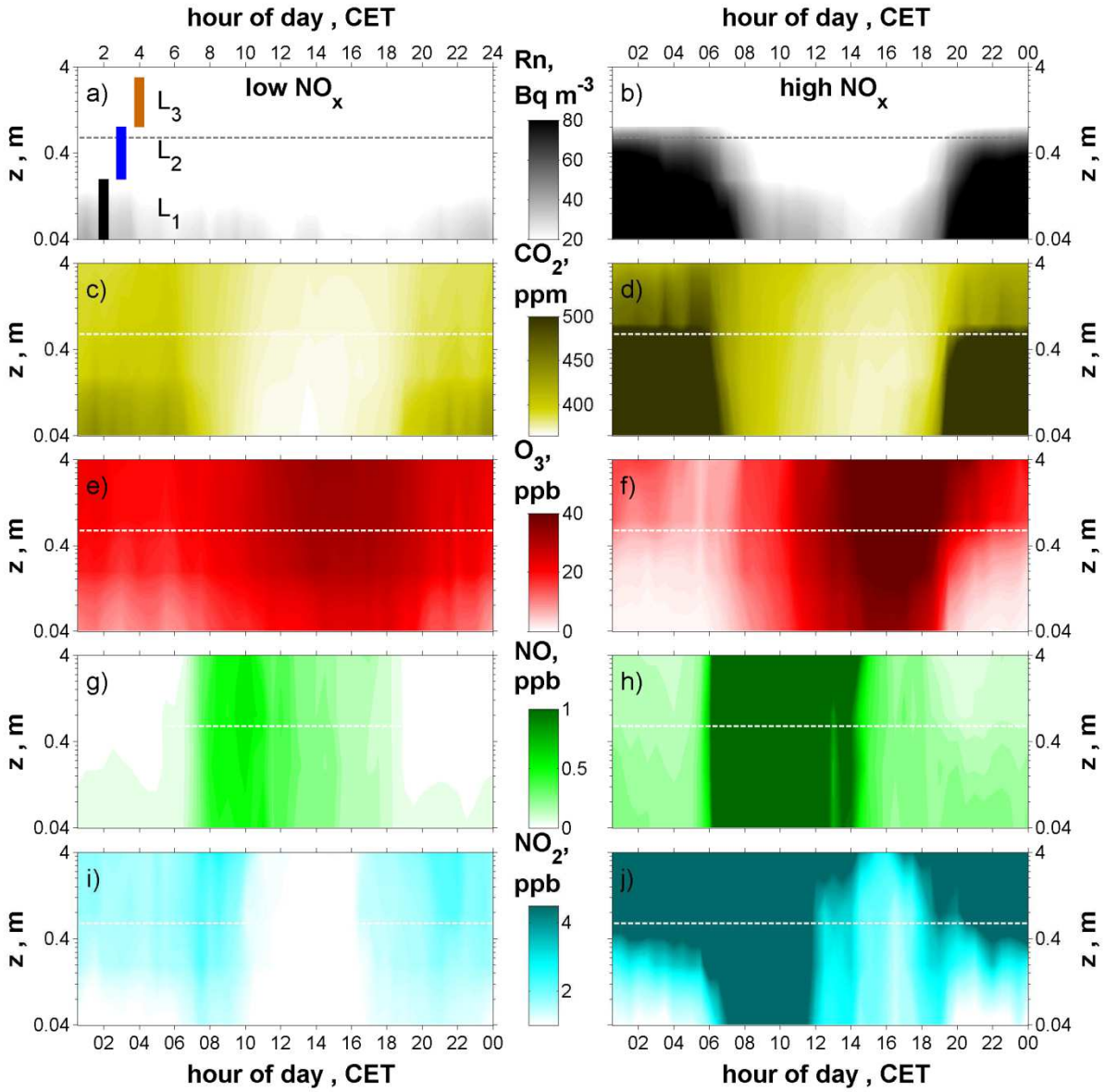

Fig. 2. Time height cross sections indicating the median vertical distribution of (a,b) Rn, (c,d) CO_2, (e,f) O_3, (g,h) NO and (i,j) NO_2 during low NO_x (left panels) and high NO_x (right panels) conditions at the Mainz-Finthen grassland site. The canopy height (dotted line) and L_{1-3} are also shown. The plots were made using the *contourf* function of MATLAB.

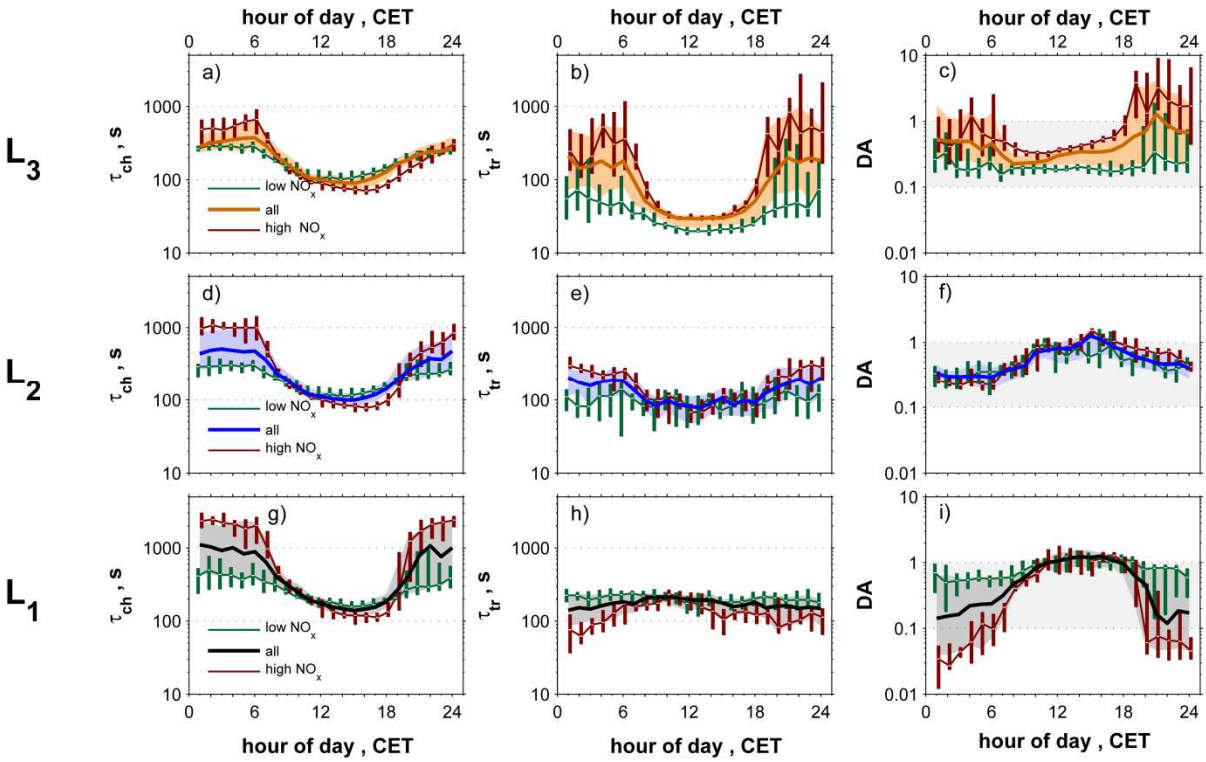

Fig. 3. Diurnal courses of (a, d, g) $\tau_{ch}(L_{1-3})$, (b, e, h) $\tau_{tr}(L_{1-3})$ and (c, f, i) $DA(L_{1-3})$ considering all data from 19 August to 26 September 2011 (medians and shaded interquartile ranges) and the low NO_x and high NO_x periods (green and brown medians and interquartile boxes) at the Mainz-Finthen grassland site.

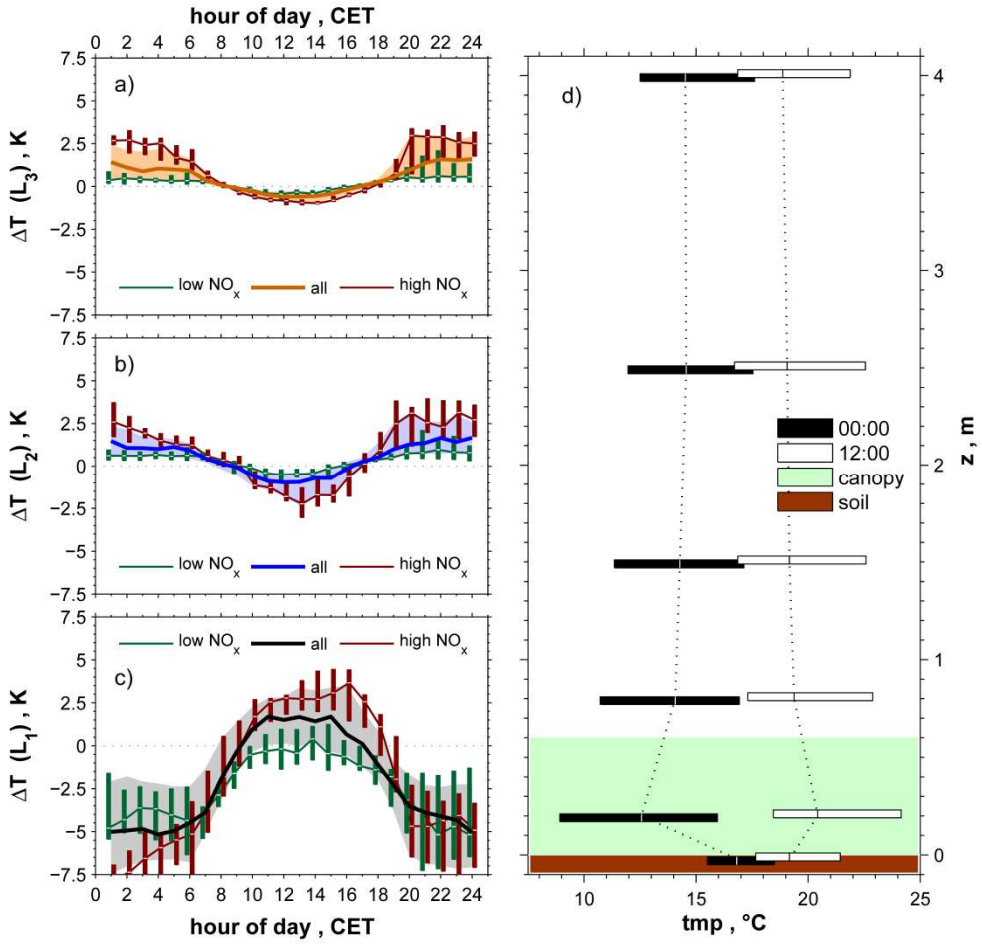

Fig. 4. (a)–(c) Diurnal courses of measured $\Delta T(L_{1-3})$ considering all data from 19 August to 26 September 2011 (medians and shaded interquartile ranges) and the low and high NO_x periods (green and brown medians and interquartile ranges); note: $\Delta T(L_1, L_3)$ do not fully cover L_1 and 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.

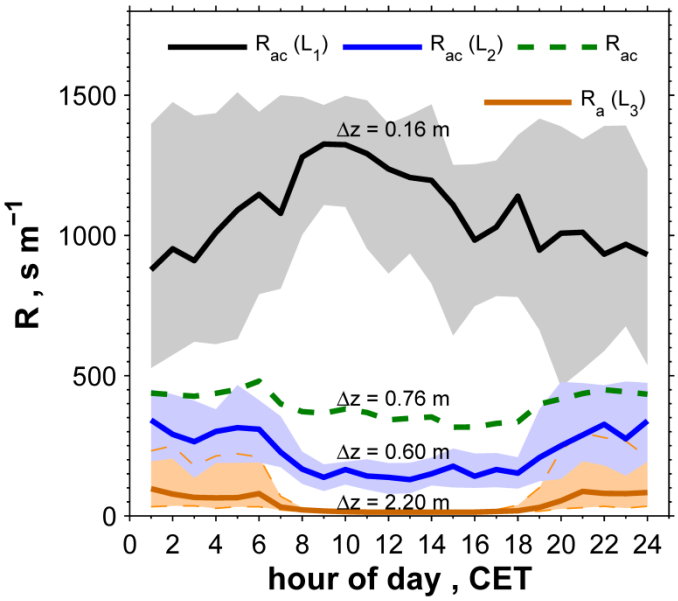

Fig. 5. Diurnal courses of in-canopy aerodynamic resistances for each individual canopy layer ($R_{ac}(L_1)$, $R_{ac}(L_2)$) and for the entire grassland canopy ($R_{ac} = \frac{\tau_{tr}(L_1)+\tau_{tr}(L_2)}{z_3-z_1}$) at the Mainz-Finthen site (median and shaded interquartile ranges). For comparison, the aerodynamic resistance above the canopy is also displayed ($R_a(L_3)$). The layer thickness (Δz) is indicated. The plot~~s~~ includes all data from 19 August until 26 September 2011.

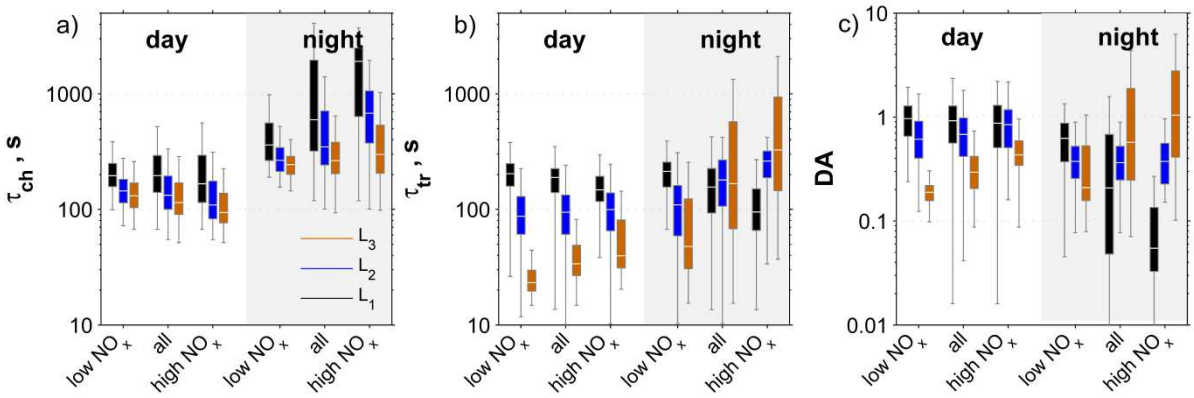

Fig. 6. Comparison of box plot statistics for $\tau_{ch}(L_{1-3})$, $\tau_{tr}(L_{1-3})$ and $DA(L_{1-3})$ during daytime and nighttime including all data from 19 August until 26 September 2011 separated for the low and high NO_x periods at the Mainz-Finthen grassland site.

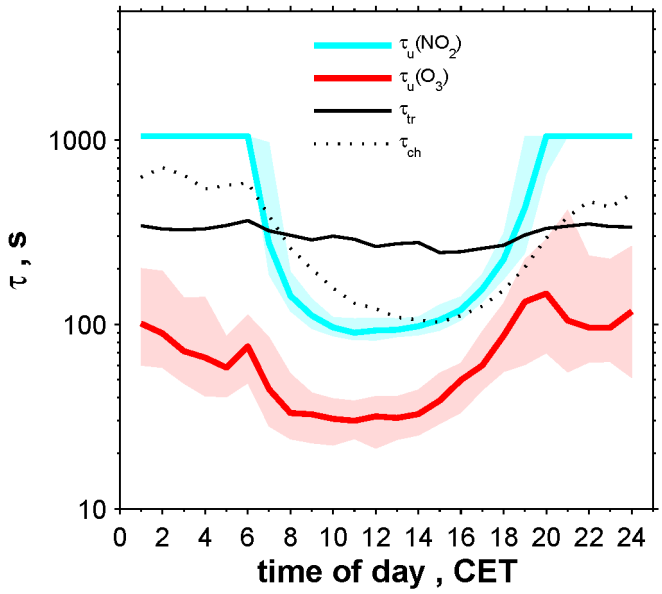

Fig. 7. Comparison of median diurnal $\tau_u(NO_2)$, $\tau_u(O_3)$, τ_{tr} and τ_{ch} with interquartile ranges for the whole canopy layer (L_{1+2}) considering all data from 19 August to 26 September 2011 at the Mainz-Finthen grassland site.

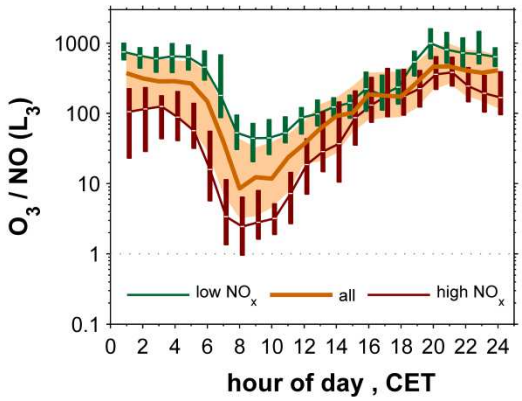

Fig. 8. Diurnal course of the O_3 to NO ratio in L_3 considering all data from 19 August to 26 September 2011 (median and shaded interquartile range) and separated for the low NO_x and high NO_x periods (medians and interquartile boxes) at the Mainz-Finthen grassland site.

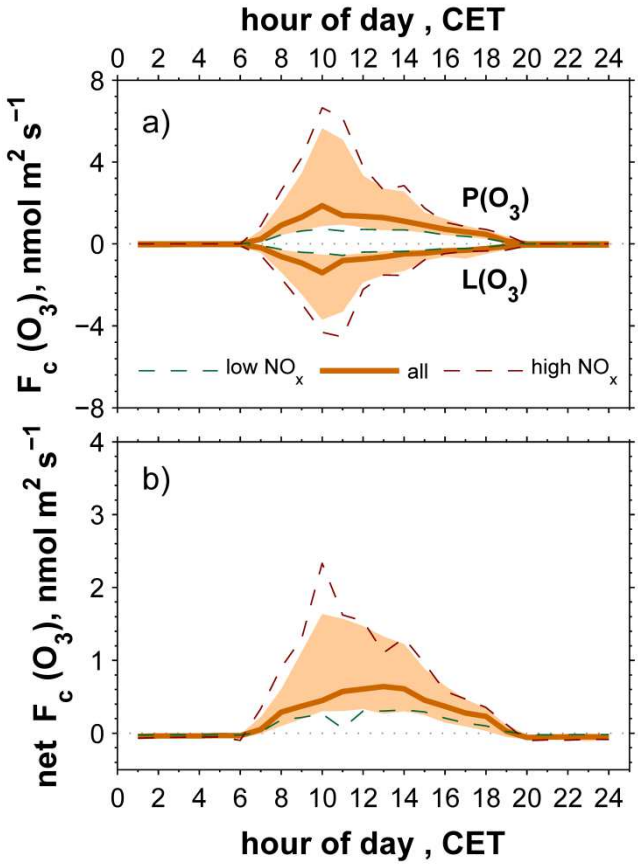

Fig. 9. Diurnal courses showing (a) $P(O_3)$ and $\mathrm{L}(O_3)$ and (b) $F_c(O_3)$ (Eq. 11) for L_3 considering all days from 19 August to 26 September 2011 (medians and shaded interquartile ranges) and separated for the low and high NO_x periods (medians) at the Mainz-Finthen grassland site.