

Dear Referee#1,

We would like to acknowledge you for your interest and the evaluation of our study. You will find hereafter our answers to your comments.

Sincerely yours,

Patrick Stella, on behalf of all co-authors.

As described by the authors, the NO, O₃, and NO₂ analyzers were located in an air conditioned container about 60m north-east from the air inlets. The non-active PFA tubes were about 62-65 meters. When air passing through the tubes from the sampling site to the analyzers, was there any change in the concentrations of NO₂ between inlets and outlets? That is, if NO react with O₃ to form NO₂ while the air passing through the tubes, observed NO₂ would be higher than it really was. This way one would find that less NO₂ deposition and elevated resistance.

As pointed out by the Referee, NO₂ mixing ratio measured by the analyzer may indeed be higher than the mixing ratio at the inlet due to the reaction between NO and O₃ (NO₂ photolysis being negligible since the tubes were opaque (p. 4469, l. 9)). This underestimate could lead in turn to an overestimate of the deposition velocity, and therefore, to a wrong estimate of the internal leaf resistance.

However, the pressure in the tubes after the critical orifice is <500 hPa and decreases to very low pressures in the instrument. Thus an average pressure of about 250 hPa may be assumed. This reduces the chemical reaction rate of O₃ with NO (compared to atmospheric pressure) by a factor of 16. In order to calculate the true concentrations and vertical profiles (used to calibrate the EC fluxes, see manuscript) measured values were corrected for the gas-phase-chemistry during the residence time of the air inside the sampling system (Beier and Schneewind, 1991). In addition, not the average change in concentration would be a potential problem for the NO₂ flux, but the change in the fluctuations (correlated with w). In the present case the turbulent fluctuations of O₃ and NO are negatively correlated (because of opposite flux directions), and thus the fluctuations of the product term [NO]x[O₃] tend to be dampened.

For the impact of chemical reactions, the authors only considered the NO-O₃-NO₂ triad. We know that there would be emission of BVOCs from the meadow. Some VOC species would react fast with O₃. Were there any differences in the chemical reactions if the role of VOCs were considered?

We fully agree with the referee that BVOCs could be emitted from the meadow and may potentially lead to O₃ destruction or production, and also to NO₂ production and NO

destruction. However, we would like to point out that beside the term “BVOCs”, there are a large variety of species with different reaction rates with O₃. Indeed, as indicated in Atkinson and Arey (2003), the lifetime of BVOCs for the reaction with O₃ ranges from few minutes (e.g., α -Terpinene, α -Humulene, β -Caryophyllene) to several hours/months (e.g., isoprene, acetone, methanol). In addition, the quantity of each compound is highly variable although BVOCs in the troposphere are dominated by methane and methanol (Jacob et al., 2005; Custer and Schade, 2007). Consequently, an evaluation of the weight of chemical reactions involving VOCs without knowledge of the species and their concentrations at our site is extremely difficult. We added in the revised manuscript the following paragraph at the end of the Section 3.4 (“Impact of chemical reactions on NO₂ fluxes):

“Besides NO-O₃-NO₂ chemistry, other reactions could induce chemical divergence especially those involving biogenic volatile organic compounds (BVOCs). BVOCs are emitted from vegetation (Guenther et al., 2000; Karl et al., 2001; Beauchamp et al., 2005; Goldstein and Galbally, 2007), including a large variety of compounds (e.g., isoprene, monoterpenes, sesquiterpenes, acetone, methanol, ethanol) with highly variable reactivity (Atkinson and Arey, 2003; Bamberger et al., 2010; Ruuskanen et al., 2011). As indicated in Atkinson and Arey (2003), the lifetime of BVOCs for the reaction with O₃ ranges from few minutes (e.g., α -Terpinene, α -Humulene, β -Caryophyllene) to several hours/months (e.g., isoprene, acetone, methanol). Bamberger et al. (2010) reported that only methanol exhibited consistent fluxes above a grassland. Since the lifetime of methanol for reaction with O₃ is very long (> 4.5 years; Atkinson and Arey, 2003), we expect a negligible impact of BVOC chemistry on NO, O₃ and NO₂. This hypothesis is also supported by the good agreement between measured and modelled NO₂ mixing ratio above the canopy (Fig. 7b).”

References

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