**Atmospheric
Chemistry
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Discussions**

Interactive comment on "Vertical advection and nocturnal deposition of ozone over a boreal pine forest" *by* Ü. Rannik et al.

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The anonymous referee addresses many important issues.

First, he/she suggests separate the chemical term in Eq. (4). What we call the total flux is most commonly defined as the total source/sink term strength inside control volume bounded from above by the EC measurement level. We follow the suggestion and write the equation in more common terms replacing the term F with the sum of vertically integrated canopy and soil source/sink term and the airborne chemical sink terms. Note that the surface deposition of ozone consists in turn of stomatal and surface depositions, which involves surface chemical reactions. The contributions of these two surface deposition mechanisms are not separated in our study and the chemical sink terms will include only chemical reactions in air.

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Turbulent transport times denote the average time of transport of air parcel from sinks (as approximated by LAD) to the flux measurement level. Thus it is the average turbulent transport time and not the chemical life-time of zone. Calculating the turbulent transport time we are able to estimate if certain chemical species are able to react in significant amounts with ozone during the transport from sources to measurement level and therefore be a chemical sink for ozone. If the reaction time of a species is much longer than the turbulent transport time, then the emitted species quits canopy to higher atmospheric levels without reacting in significant amount with ozone. Thus only chemical species with reaction times comparable to (or smaller than) the turbulent transport time can consume ozone below the EC measurement level.

There is no mistake in Table 1. Table 1 is the result of simulations for friction velocity 1 m/s. According to common parameterizations velocities are proportional to friction velocity and therefore transport time scales inversely proportionally with friction velocity. Therefore turbulent transport times can be rescaled to other values of friction velocity. For simplicity we have presented the simulation results in Table 1 for friction velocity 1 m/s. In the text we refer to possible variation range of the average transport time rescaled to friction velocity range from 0.1 to 0.5 m/s. We agree that this needs better explanation.

Next we summarize in brief the assumptions and calculation behind the sink estimates of ozone with reactions with sesquiterpenes and NO. First, these chemical species are supposed to have chemical life-times comparable to turbulent transport time. The most abundant sesquiterpene observed at site is beta-caryophyllene (Hakola et al., Biogeosciences, 3, 93-101, 2006). The reaction rate of this sesquiterpene with ozone is 1.16 10-14 cm3 molecule-1 s-1. With typical ozone concentration observed at site around 30 nmol/mol (30 x 10-9 moles per mole of dry air being equal to 7.5 x 10^11 molecules cm-3), the first-order time-scale for beta-caryophyllene is around 2 minutes. This is comparable to turbulent transport time as identified in paper. The other possible candidate analysed in paper NO has a reaction rate constant with ozone for night-

time conditions parameterized as $k = 2.6 \times 10^{-12} \exp(-1436/T)$, which gives for $T = 293$ K 1.9×10^{-14} cm3 molecule-1 s-1, thus being in the order of 1 minute. The other VOC's are excluded because to our knowledge there is no other VOC's with fast enough reaction time-scales to be able to cause significant sink of ozone within comparable time scales to turbulent transport time. For example, the most abundant monoterpene observed at the site alpha-pinene has a reaction rate constant 8.66×10^{-17} cm3 molecule-1 s-1, which corresponds to first-order chemical degradation time about 4.3 hours. The reaction rate for isoprene is 1.19×10^{-17} and for methylbutanol 8.3×10^{-18} cm3 molecule-1 s-1 (Klawatsch-Carrasco et al., International J. Chemical Kinetics, 36, 152-156, 2004) yield reaction time scales of 31 and 45 hours, respectively.

Thus chemical time scale analysis enables us to select chemical compounds able to react with ozone during transport time from canopy emission until EC measurement level. For simplicity and to obtain maximum impact estimate, in following we assume that all emitted sesquiterpenes and NO react below the measurement level. The sesquiterpene emission rates at the site have been estimated up to 40 mg m-2 month-1. Reacting exclusively with ozone before escaping to higher atmospheric levels would imply ozone chemical sink below EC measurement level with strength 0.1 nmol m-2 s-1. Similarly, the observed NO emission rate by 6 ng(N) m-2 hr-1 would imply ozone chemical sink with strength 10-4 nmol m-2 s-1. These are upper estimates for potential ozone sink strengths, being still negligible compared to ozone sink as estimated from the sum of the flux terms.

The night-time forest-atmosphere exchange of reactive and non-reactive gases is different. The reactive gases can be consumed by chemical reactions inside and above canopy, therefore the air chemistry can contribute to source/sink strength below the observation level. The potential of chemical reactions to produce/destroy depends on the time scale of chemical reactions relative to average turbulent transport time between sources/sinks and observation level.

The carbon dioxide is emitted and ozone deposits into forest canopy. This makes also

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a significant difference for night-time conditions. Under strongly stable conditions the emission of a substance can lead to significant accumulation inside canopy. This results in large storage term but can lead also to large horizontal as well as vertical advection terms (terms being proportional to horizontal and vertical gradients of concentration). Ozone is deposited into forest canopy and under limited turbulent transport conditions the ozone depletion leads to lower concentrations inside canopy. However, the horizontal and vertical gradients formed under such conditions can not be as large as for emitted quantity and therefore mass balance of the compound is probably less affected by advection terms.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 18437, 2008.

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