Response to the referee comments by K. Pilegaard (Atmos. Chem. Phys. Discuss., 12, C4798–C4801, 2012).

The authors thank the reviewer for the useful comments on our manuscript. The manuscript will be revised accordingly as described below. In the following we address each remark and describe the changes that will be applied to the current version of the paper.

1 General comments

The dataset presented is very impressive and in general the analysis is quite sophisticated. I miss a better analysis of the role of chemical reactions with monoterpenes and a more detailed description of other possible non-stomatal removal mechanisms and quantification of their individual contribution to the total flux.

Reply: The role of chemical reactions with monoterpenes was analysed by multi-variate statistical analysis trying to identify explaining power of monoterpene concentration (among other variables) in ozone deposition. The analysis revealed that monoterpene concentration was a significant variable explaining total and non-stomatal ozone conductances. However, known emissions of monoterpenes, considering relatively slow chemical reactions with ozone, are not able to affect significantly ozone deposition in canopy air space (see answer below to the question related to p. 12735). Therefore, it is likely that other unknown chemical compounds or processes correlating with monoterpene concentration are responsible for non-stomatal chemical sink term.

Recent in situ chemistry measurements indicate that the coniferous canopy air space possesses a large, unknown sink for OH (Sinha et al., 2010; Nölscher et al., 2012). The exponential dependence between temperature and missing OH reactivity suggests that complex reactions between the biogenic terpenes or some secondary reaction products may explain the missing OH sink. Regrettably, the models for O_3 deposition are similarly suffering from the lack of detailed knowledge of participating compounds. Acknowledging a) the limited knowledge of compounds participating in air chemistry of OH and O_3 (and their emissions), and b) known emission rates of monoterpenes at the given site and more than two orders of magnitude slower chemical reaction rates of monoterpenes with O_3, the authors are convinced that additional analysis of the role of monoterpene chemistry in O_3 sinks does not contribute to further understanding of O_3 non-stomatal sink.

Thus, the results clearly show the importance of several non-stomatal removal mechanisms, however their relative contributions are not possible to analyse from canopy-level measurements without specific knowledge on simultaneous shoot-level gas-phase concentrations.

2 Specific comments

p. 12720, l. 23: The instrument used for O_3 fluxes was an LOZ-3. How was this calibrated and what was the flux data coverage for this instrument which has a reputation of being rather delicate and not so easy to maintain on a very long term?

Reply: The instrument was calibrated as described in Keronen et al. (Boreal Environment Research, 8, 425-443, 2003), see the summary below.

The maintenance of the O_3 analyser required monitoring the amount of the reagent liquid solvent ethylene glycol and adding it at a few months interval to keep the reservoir bottle full. Also the sample pressure required monitoring because if the pressure difference against the ambient pressure exceeded 200 hPa, the reagent liquid flow rate increased too much so that the re-circulation function failed. The filter at the analyser inlet was changed at a few months' intervals during other service/repair work.

Regular calibration checks included checking the span coefficient and zero offset. For determining the span coefficient the ambient O_3 concentration, measured by an ultraviolet photometric analyser (TEI 49, Thermo Environmental Instruments Inc., Franklin, MA, USA) at height 16.8 m at the station, was used as the reference. The TEI 49 analyser is calibrated regularly against a transfer standard photometer (Dasibi 1008 PC, Dasibi Environmental Corp., Glendale, CA, USA), which in turn is calibrated at the Finnish Meteorological Institute against the Ozone Photometer (S/N 63718-341) traceable to the Standard Reference Photometer (SRP #15, Certificate No 01/2, 12.7.2001, EMPA). For determining the zero offset the analyser's internal activated carbon containing scrubber was used to purify the sample air. Because the span stability of the O_3 analyser was observed to be drifting quite a lot it was decided that the calibration should be checked weekly. This way the span stability could be kept within the ±10 % value.

p. 12723, l. 7-9: I am not sure what is meant here. Should it be “calculated” rather than “accounted (for)”?

Reply: It was meant that variations in parameter α can equally well describe changes in stomatal conductance (model output) when actually (or presumably) λ varies. Thus from the modelling point of view λ can be kept constant during the whole season, respective impact to model output being incorporated in variation of α. This will be better explained.

p. 12725, sect. 2.3.3: This section only deals with sesquiterpenes. How was the chemical reactions with monoterpenes dealt with?

Reply: The monoterpenes were not directly included in the analysis, see answer to General comment and question related to p. 12735 below.

p. 12726, l. 5: What was the reason for the longer measurement break? What was the overall coverage for O_3 flux data?

Reply: The reason for longer measurement break in 2006 was technical problems. During reparation some hardware of the instrument was replaced and additional monitoring measurements were implemented. The problems started in Dec. 2005 and the instrument was finally repaired and installed in Dec. 2006.

Ozone flux data coverage was as presented below. This will be reported in revised manuscript.

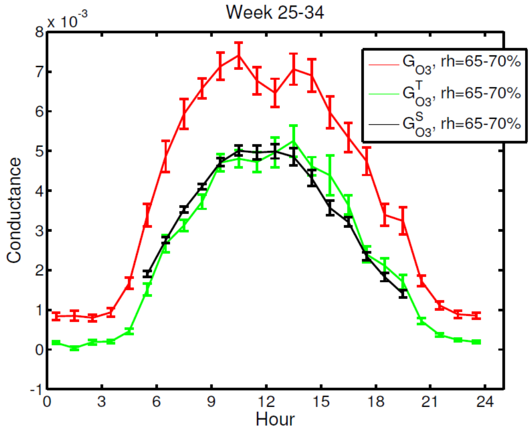
Year	**Flux data coverage (%)**
2001	20.4
2002	59.5
2003	72.1
2004	71.7
2005	71.9
2006	0.0
2007	52.0
2008	73.2
2009	73.8
2010	57.2

p. 12726, l. 13: In addition to fig. 2, I suggest to add a figure showing the average annual variation in the O_3 concentration (relevant for the statement given in l. 7-9 on the same page).

Reply: Figure 1, representing the time series of ozone fluxes and concentrations over period of measurements, gives also idea of the average annual variation of ozone concentration. Adding additional figure would be partly repetition. We prefer to keep Figure 1 in its current form.

p. 12727, l. 19-20: How did $G^S_{O_3}$ and $G^T_{O_3}$ compare around RH_ 70%?

Reply: The comparison of $G^S_{O_3}$ and $G^T_{O_3}$ is presented on the following figure for humidity interval from 65 to 70 %, for the peak growing season.



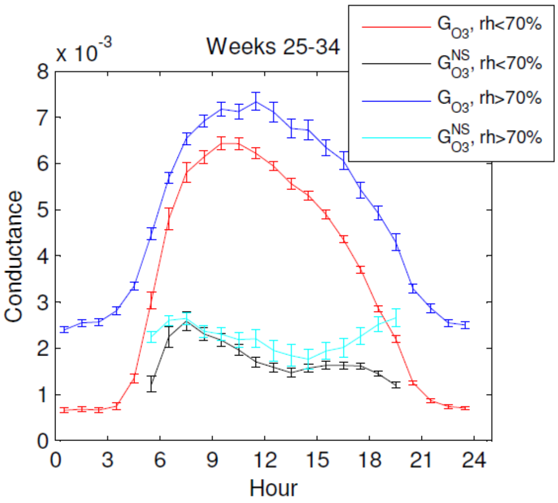
In general those conductances compared very well except during the spring recovery period (weeks 15-19), when conductances inferred from water flux measurements exceeded the model values. This period corresponds roughly to April when snow thawing presumable has contributed to water fluxes and resulted in overestimation of $G^T{}_{O3}$.

p. 12728, l. 3-5: Does the lack of a diurnal variation during the dormant period mean that there is no temperature influence on the non-stomatal uptake? This is a bit in contradiction to the statement on p. 12731, l. 29, where temperature is identified as an important variable for non-stomatal conductance.

Reply: The non-stomatal deposition mechanisms can be different during dormant and growing season periods. The statistical analysis was performed only for growing season period (this will be more clearly stated in the revised manuscript). Thus there is no contradiction in results.

p. 12728, 6-13: Is there a diurnal variation in the non-stomatal O_3 conductance? Or is the diurnal variation in total O_3 conductance only due to the variation in the stomatal conductance?

Reply: Indeed, the manuscript does not present diurnal variation of non-stomatal conductance but only the fraction of non-stomatal conductance relative to total conductance. Diurnal variation of non-stomatal conductance is presented below for peak growing season, which characterises also the other seasons. The non-stomatal conductance is generally smaller at noon and higher in the morning and in the afternoon. This will be shortly discussed in the revised version.



p. 12735: The paper presents a detailed analysis of the role of chemical reactions with sesquiterpenes, but it seems that a similar analysis of the role of monoterpenes is missing. The conclusions made about reactions with monoterpenes as an important removal mechanism is based on the multivariate analyses only. Would it be possible to simulate reactions with monoterpenes in the same way as for sesquiterpenes?

Reply: Simulation of reactions with monoterpenes does not add new information. Instead, an order of magnitude estimation and discussion will be included.

The emission potential of β-caryophyllene (as the representative sesquiterpene) is varying at the site and is reported to range from 160 to 380 ng g^{-1}(dw) h^{-1}. The emission potentials for dominant monoterpene, 3-carene, have been reported to be 4000 ng g^{-1}(dw) h^{-1} in early summer at its maximum, total monoterpenes being represented by 5200 ng g^{-1}(dw) h^{-1} (Tarviainen et al., Biogeosciences, 3, 93–101, 2006, Atmos. Chem. Phys., 5, 989–998, 2005; Hakola et al., 2006). Thus, emission potential of monoterpenes is approximately an order of magnitude larger than that of sesquiterpenes. However, the reaction rates of β-caryophyllene and 3-carene with ozone are $1.2x10^{-14}$ and $4x10^{-17}$ cm^3 $molec^{-1}$ s^{-1}, respectively, differing by more than two orders of magnitude. Based on this knowledge monoterpenes, as represented by dominant compound 3-carene, cannot by a significant non-stomatal sink inside canopy air space.

This observation was also supported by Rinne et al. (Atmos. Chem. Phys., 12, 4843–4854, 2012), who found that more than 90% of monoterpene α-pinene escaped canopy at night, with respective figure being close to 100% during day-time. Thus our current knowledge of monoterpene emissions does not support their significant role in ozone degradation inside canopy air space.

p. 12737: I suggest that the conclusion part try harder to describe the quantitative role of the different non-stomatal sinks. I find that the last sentence is a bit weak.

Reply: The conclusions on the role of different non-stomatal sinks can be only indirect conclusions based on the presented analysis. The results clearly show the importance of several non-stomatal removal mechanisms. Recent in situ chemistry measurements indicate that the coniferous canopy air space possesses a large, unknown sink for OH (Nölscher et al., Atmos. Chem. Phys. Discuss., 12, 7419–7452, 2012). This study suggested that complex yet unknown reactions between the biogenic terpenes or some secondary reaction products may explain the missing OH sink. The models for O_3 deposition are similarly suffering from the lack of detailed knowledge of participating compounds and therefore more reliable quantification of compounds participating in O_3 chemistry cannot be done.

In summary, the analysis revealed that monoterpene concentration was a significant variable explaining total and non-stomatal ozone conductances. This suggests indirectly that monoterpenes or compounds (or environmental variables) correlating with monoterpene concentration, but not directly accounted for in multi-variate analysis, have a relation to ozone deposition. However, known emissions of monoterpenes, considering relatively slow chemical reactions with ozone, are not able to affect significantly ozone deposition in canopy air space. Therefore, it is likely that other unknown chemical compounds or processes correlating with ozone deposition rates, including potentially reactions at the surfaces, are responsible for non-stomatal chemical sink term. This will be more clearly stated in revised manuscript.

3 Technical comments

p. 12717, l.26: There is a significant lack of indefinite and definite articles in the manuscript. Here is an example, where I have added articles in bold: “... noted that **the** life-times of many reactive terpenes can be less than a minute and **a** significant part of **the** ozone deposition into **the** ecosystem ...” The lack of definite and indefinite articles throughout the manuscript is probably due to the fact that they are not used in the Finnish language. I therefore suggest that the authors send the manuscript for language revision by a person with English as his/hers native language.

Reply: The manuscript will be revised for language errors.

p. 12718, l. 9: change to “...that there **are** various mechanisms...”

Reply: To be corrected.

p. 12719, l. 4: ‘‘results in” rather than “present”

Reply: To be corrected.

p. 12725, l. 3-5: The sentence starting with “The stomatal conductances ...” is redundant. The information was already given a few lines above (p. 12724, l. 22-23)

Reply: To be removed.

p. 12735, l. 18: “ponderosa” instead of “Ponderosa”.

Reply: To be corrected.