Response to the referee comments by Laurens Ganzeveld (Atmos. Chem. Phys. Discuss., 12, C4536–C4536 , 2012).

The authors thank the reviewer for the constructive comments on our manuscript. The manuscript will be revised according to these comments as described in detail below. In the following we address each comment and emphasize the changes that will be applied to the current version of the paper.

Comment: Line 23: "Several papers addressing the ozone deposition over pine forests (Goldstein et al., 2004; Holzinger et al., 2005, 2006) revealed the role of oxidation products of biogenic emissions in ozone removal". You are stating here that the oxidation products of BVOC emissions are explaining the removal of ozone but checking again for example the Holzinger et al., 2005 reference it is actually been postulated that the oxidation products are indicating the role of BVOC-ozonolysis reactions.

Reply: Correct. Goldstein et al. (2004) observe that thinning of ponderosa pine plantation enhanced both monoterpene emission and ozone uptake and conclude that these simultaneous enhancements provide strong evidence that ozone reactions with unmeasured biogenically emitted volatile organic compounds (BVOCs) dominate ozone uptake. Holzinger et al. (2006) observe indirect connection between non-stomatal ozone and monoterpene flux and suggest that also along with the emission of monoterpenes large amounts of other substances are released that react with ozone and cause the observed chemical non-stomatal ozone flux. Holzinger et al. (2005) suggest that biogenic emissions of precursors oxidize with ozone. The statement will be corrected.

Comment: Section 2.3.2 Bulk canopy conductances;

Reading through this section in which the analysis of the observations in terms of the stomatal and non-stomatal components is being explained the question is raised on how the aerodynamic and quasi-laminar transfer contributions have been considered in the analysis. This seems to be one of the major flaws of the presented study (or you have a good reason to leave it out and simply didn't include it in the ms).
You calculate the stomatal and non-stomatal conductances from the measured flux but this conductances then include also the (inverse of) the aerodynamic- and quasi-laminar resistance terms. I am aware that these terms are generally less important in the total transfer pathway but can become relevant especially at days with efficient stomatal (or non-stomatal) uptake. Consequently, this has be modified in the revised version of your ms.

Reply: The stomatal conductance calculated from the multi-layer model corresponded to a value at the canopy top. When stomatal conductance was inferred from water flux measurements, then aerodynamic resistance was accounted according to eq. (A12). Deposition route for non-stomatal component is not fully clear. Non-stomatal sink at needle surface includes quasi-laminar resistance but if the non-stomatal sink is caused by chemical reactions in the canopy air space, the quasi-laminar resistance is irrelevant. While doing the analysis we accounted for quasi-laminar resistance according to eq. (A5) and compared the results. Since no difference was observed, we defined the stomatal as well as non-stomatal bulk conductances at the canopy top, accounting with the aerodynamic resistance but neglecting the quasi-laminar resistance. We are confident that this does not have effect on results.

Comment: In the section on the ozone chemical modelling is becomes clear after some reading that you apparently use here also a vertical layering system in which you calculate the concentrations and fluxes using an iterative system. I haven't read any information up to this stage on the resolution of your vertical layering. What is the selected thickness of the vertical layers of your multi-layer uptake and chemical destruction model system?

Reply: We have used 50 layers inside canopy, thus the thickness being 0.02 H (canopy height). We will add this information into updated manuscript.

Comment: Page 12725, line 22; "In order to solve concentration and flux profiles simultaneously for ozone and B-caryophyllene, **an** iterative method was used with **the** measured ozone concentration at the canopy top **being used as** the boundary condition. For vertical integration **a** numerically stable forward Eulerian scheme was applied (also with iterative correction at each level) and zero-caryophyllene flux assumption at upper boundary of the simulation domain was superimposed" (this comment might reflect a difference of "taste" on UK writing styles. It addresses the fact that according to my opinion the overall document should be carefully checked for having left out too many times "the" and "a/an" terms).

Reply: The manuscript will be revised for language errors.

Comment: What is meant with an iterative correction at each level?

This is a numerical detail with little interest. We used forward Eulerian scheme in integration as a first step at each level and then corrected the calculation for the same level with Eulerian backward scheme calculation to improve accuracy.

Comment: Line 29: "Since no sensitivity of the results **to the assumption on** atmospheric boundary layer (ABL) height was observed from the model runs the ABL height was set for simplicity to 300 m". This remark also raises the question of your selected vertical layering system that apparently goes all the way up to 300m or ?

Reply: The vertical layering was used up to 300 m only for the calculations of the impact of sesquiterpene emissions on ozone flux. In calculation of stomatal ozone conductance by multi-layer model integration was performed only up to the canopy top.

Comment: Page 12726: "In 2006 **there has been a relative** long **break in the** measurement **record**", how long was it, some months??

Reply: The break was from Dec. 2005 till Dec. 2006 altogether approx. 13 months.

Comment: Line 7; "It is important to note that **the** flux is" (after this I stopped adding the terms "the or a/an", this should be done by the authors/text editors at the Copernicus office)

Reply: See answer above regarding language revision.

Comment: Page 12727, line 13:14, you mention that the analysis is limited to daytime conditions, which is understandable if you want to focus on the stomatal versus the non-stomatal uptake (and assuming that there is complete night-time stomatal closure). But what is your justification for only using data with sufficient turbulence? Under conditions with relative small turbulence the chemical timescale might get even closure to the turbulent timescale implying an even more important role of chemistry in O_3 deposition.

Reply: The criterion $u_* < 0.1$ m s^{-1} was used to exclude conditions with very weak turbulence, which frequently are characterized by large random errors and non-stationarity. On the other hand during day-time such conditions rarely occur and we believe that results are not affected by this selection threshold.

Comment: Page 12728: line 14. In contrast to what your extensively expressed previously you actually include here in the analysis nocturnal O_3 deposition. I think this is very interesting and like to see this included in the analysis but you should modify the previous statements saying that your analysis "focusses on daytime deposition"

Reply: Correct. Our main focus was on day-time measurements but we shortly presented also night-time results. We will revise the statement on the focus so that it would not confuse.

Comment: Page 12729; "Further, variation of total and non-stomatal conductance as a function of relative humidity (RH), temperature and photo-synthetically active radiation (PAR) was studied". In the sentence before you state that the non-stomatal component also depends on turbulence, which is obvious thinking about the role of turbulence in mixing in O_3 into the canopy space where it reacts with emitted terpenes but where the turbulence might also play an important role in efficiently transporting the O_3 all the way down to the soil surface where deposition can be another important contributor to the non-stomatal uptake term. Why do you limit your analysis to the role of PAR and RH?

Reply: The sentence before states general expectation that environmental variables including friction velocity affect ozone deposition. Later, line 14 of the same page, we state that friction velocity did not exhibit impact on ozone deposition. Thus, actually we studied but we did not find correlation between ozone deposition flux and friction velocity. We will revise the paragraph to avoid confusion.

Comment: And then read the following sentence: "Friction velocity did not exhibit clear impact on O_3 deposition (not shown).". Still it is interesting to consider why there is apparently no dependence on u* since you would expect such a dependence.

Reply: We did not observe dependence of ozone conductance (also non-stomatal) on friction velocity. Such a dependence would be expected in case of chemical reactions if turbulent transport time would be in the same order as the chemical reaction time scale. Nevertheless, dependence of deposition on friction velocity was not observed.

Comment: Page 12730: "At night the conductance inferred from water flux measurements G^T_{O3} was used as a surrogate to estimate stomatal deposition during dry periods.". Maybe I missed something but this is not completely clear to me. Why using the nighttime conductance to estimate stomatal deposition during dry periods? Are you referring here to nighttime stomatal deposition (which I thought you were assuming that this is not happening having said that you focused on daytime data which apparently is not the case seeing also this section 3.2.2 on nighttime deposition)

Reply: The main focus of the study was on day-time analysis. However, we looked also night-time total ozone conductance as well stomatal conductance at low RH (inferred from water flux measurements). We are not making assumption that night-time stomatal conductance is zero.

Comment: Page 12731: line 19 "Comparison of the measurements and predictions enables to conclude that (i) **the** environmental variables **that have been included in the presented analysis** were able to predict ~~similar variation with~~ **to large extent the** observed **variability** during the course of the year, i.e. the seasonal variation with 98% of the variance **being** explained but (ii) failed to explain pattern in inter-annual differences (only 8% of the variance explained) such as elevated G_{O3} during the weeks 33–35 in 2005, systematically lower G_{O3} during the weeks 35–39 in 2008 (Fig. 8a)." This sentence is not well readable and since it is an important finding it should be revised to make the statement very clear (already put some suggestions for textual change)

Reply: Thank you, we will revise the sentence.

Comment: In section 3.4 you analyse the role of terpene emissions in explaining to some extent the non-stomatal O3 deposition. Previously you shortly mentioned the role of soil NOx and was wondering if you actually considered to include this in your multi-layer model calculation to assess the contribution by the NO-O3. On the other hand, then your model can so easily become so complex and then you would need an explicit multi-layer exchanges model that considers the full suite of canopy interactions.
What are anyhow the NO emission fluxes at the site and how much could they contribute to O3 deposition associated with NO titration?

Reply: The possible role of NOx emissions on ozone non-stomatal sink is shortly discussed in Section 4 (page 12734 line 27 onwards). We do not believe that NOx emission constitutes a significant ozone sink term. The multi-variate analysis did not also indicate correlation between NOx concentration and ozone deposition. The NOx emission fluxes at the site are very low. According to measurements at site both N_2O and NO were emitted from the soil and NO_2 was deposited into the soil. Annual cumulative soil N_2O emission averaged to 0.3 $kgNha^{-1}\ yr^{-1}$. Measuring NO emission and NO_2 deposition from/to the soil was challenging at the site because of the small fluxes. During the campaign in the autumn period 2011 measured NO-N emission was around 0.01 $kgNha^{-1}\ yr^{-1}$ and NO_2-N deposition was even smaller. More information can be found in Biogeosciences, Discuss., 9, 11201-11237, 2012.

Comment: Page 12732; "It is noteworthy that for O3 the vertical divergence of the turbulent flux cannot be disti**n**guished from stomatal sink term". This is very interesting finding on the role of the chemistry in the explaining ozone deposition for this site. Since not all readers might be informed about the issue of flux divergences associated with chemistry and why this expresses it might be worthwhile to consider to explains this in a little more detail. Anyhow, so this finding indicates that the flux divergence due to chemistry cannot be distinguished from the stomatal uptake implying that chemistry overall plays a minor role. Still we have seen quite some important role of non-stomatal uptake which apparently then is also not very strongly determined by in-canopy chemistry but more likely by a suite of other processes (soil uptake, thermal decomposition, etc.)

Reply: We will explain shortly about the meaning of flux divergence and how it would be related to chemical sink term. The result indicates that β-cayophyllene in expected emission quantities does not constitute a significant ozone sink.

Comment: Page 12734: "but failed to explain major inter-annual differences". I think this is a really interesting finding. You would expect that some extent these inter-annual differences would have to do with controlling parameter that respond on relative long timescales (seasons/years). The potential parameters that operate at these timescales are soil moisture status and phenology but somehow these have been considered in your analyses. It raises the question if these have been properly included in your analyses which appears now to be done through the adjustments of your stomatal model scaling parameters. What other long-term parameter variability explains O_3 deposition?

Reply: Yes, we included phenology (via parameter α of the optimal stomatal model that was obtained from canopy level carbon dioxide and water fluxes) and soil water content in the multi-variate analysis. We believe that the parameter α is well estimated and characterises canopy photosynthetic capacity. Soil temperature is also a slowly varying parameter, but does not perform as a significant parameter in terms explaining power of ozone deposition. We do not know why the inter-annual variability in ozone deposition is poorly explained. It could be due to episodic events that are not described by the set of explaining variables used in our study.

Comment: You raise the issue on the role of soil NO but this source is simply too small to have a significant impact on O_3 deposition. In addition the isoprene-O_3 reaction is also to slow (compared to OH-isoprene) to have a significant impact.

Reply: Yes, we agree.

Comment: Page 12735; the discussion on the role of BVOCs in explaining the O_3 deposition is too much repetition of what was already presented in the introduction.

Reply: We will check the introduction and respective discussion parts for repetition and revise.

Comment: Page 12736: "The multivariate analysis did not reveal dependence of O_3 total and non-stomatal conductances on turbulence intensity. Turbulent transport time is directly related to turbulence intensity and the ratio of this time-scale to chemical reaction-rate time-scale should affect the non-stomatal deposition". This comment also raises the question about the calculations in-canopy turbulence in your study. You indicated that this relies on the use of the K-theory which we know generally fails in reproducing observed turbulence properties inside the roughness layer and the canopy. So, your estimates of the turbulent timescales might be not very optimal. But so you would anticipate them to be even shorter likely further reducing the role of chemistry in O_3 deposition. You can have a look on the sensitivity to some of these canopy exchange features to the representation of canopy turbulence but then with a focus on BVOC exchanges in a paper by Bryant et al. (acpd-2012-137) also currently in the discussion stage of ACPD.

Reply: We are aware that K-theory in general fails to describe all features of canopy exchange processes, including counter-gradient fluxes. However, we believe that it is a sufficiently good tool for the current purposes where the idea is to estimate what fraction of ozone reacts with a sesquiterpene during its transport pathway from above canopy to sink locations inside canopy. For example, we calculated that approximately 40% of emitted β-caryophyllene escaped canopy. Rinne et al. (Atmos. Chem. Phys., 12, 4843–4854, 2012) has used the Lagrangian Stochastic dispersion model, free of the limitation of K-theory based models, to evaluate the impact of chemistry on BVOC fluxes and found similar value. Thus we believe that K-theory based model is sufficient for the present purpose.

Comment: Furthermore, analysis of the role of chemistry, which is limited in your analysis to the role of caryopyllene, might need to be modified including a whole suite of very reactive compounds (represented in a generic way) recognizing the fact that observations of OH reactivity at the SMEAR site suggest much more reactive compounds being present than the ones that we can currently consider in such model analysis based on observed BVOC emissions (Nölscher et al., ACP special issue on HUMPPA/COPEC campaign)

Reply: The known emissions of BVOC at the given site consist mainly of monoterpenes and sesquiterpenes. The selected sesquiterpene β-carophyllene has significantly faster reaction rate with ozone compared to monoterpoenes. Thus we expected that chemical sink due to known monoterpene esmissions cannot be a significant ozone sink.

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 and therefore we do not expect that more complicated model calculations involving a wide range of reactive compounds would yield better understanding compared to single case study with β-carophyllene. The reaction coefficient between O_3 and the selected sesquiterpene (caryophyllene) is three magnitudes higher than that with monoterpenes, which implies that for O_3, the simple model including degradation by reactions with caryophyllene may not be as far off.

Comment: Page 12737; “It was concluded that chemical reactions with monoterpenes, or other removal mechanisms such as surface reactions, play a role as ozone non-stomatal sink inside canopy”. I think that your concluding sentence (and some previous remarks) need to some re-writing. This conclusion is not very convincing. It is also because you wonder based on the discussion how the monoterpenes can be important as an non-stomatal sink whereas these much less reactive compared to the sesquiterpenes and these do not appear to play a role in ozone deposition. Is it then at the end the fact that the monoterpene emissions are substantially larger?? But the role of monoterpenes in O3 deposition depends on the chemical timescale relative to the deposition timescale and this latter is generally short compared to the monoterpene-O_3 chemical timescale.
Finally, I would actually suggest to include also here a statement about the rather surprising missing role of turbulence in the non-stomatal uptake but also this finding that apparently some still unknown mechanisms might be involved in determining inter-annual variability.

Reply: Thank you for suggestion. We will revise our conclusion. Multi-variate analysis revealed that monoterpene concentration was a significant variable explaining total and non-stomatal ozone conductances. This seems to be in contradiction with the fact that known emissions of monoterpenes, considering relatively slow chemical reactions with ozone, are not able to affect significantly ozone deposition in canopy air space. This suggests indirectly that other compounds (or environmental variables) correlating with monoterpene concentration, but not directly accounted for in multi-variate analysis, have a relation to non-stomatal ozone deposition. This will be more clearly stated in revised manuscript.

We will include in the conclusions the observation that friction velocity was not observed to be related to non-stomatal deposition. Also the fact that inter-annual variation was poorly explained by used environmental factors and concentrations.