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Comment

## ***Interactive comment on “Plant surface reactions: an ozone defence mechanism impacting atmospheric chemistry” by W. Jud et al.***

**Anonymous Referee #2**

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The manuscript contribute to the state of the art, suggesting that previous research may have overestimated stomatal sink of ozone because surface reactions with O<sub>3</sub> were not considered. This finding should be cautiously considered because only few plants emit very reactive VOC such as diterpenoids. There are several methodological flaws which should be fixed in order to ameliorate the robustness of the research. The authors should clearly show the total O<sub>3</sub> flux measured in the cuvette and compare the relative contribution of stomata vs surface deposition. A graph showing total ozone fluxes and (estimated) stomatal ozone fluxes for each cultivar may help to better understand the results and convince the reader. The role of stomata is not fully represented, since cultivars are compared but the stomatal conductance to water vapor is not clearly shown in the figures. I am convinced that the article pushes forward the state of the

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art with an initial effort to better investigate the role of reactive VOC in the O<sub>3</sub> deposition. The paper should be published in ACP after replying these major comments: Pag 19874 lines 5-7: The striking questions assumes that poor research has been carried out to assess stomatal ozone uptake, but this is not true. The striking questions could be tuned in such a way: "Can surface reactions limit ozone entry through stomata and therefore reduce oxidative damage?" Pag. 19877 lines 5-: There is information here which should go on setup section, i.e. the enclosed leaf surface. Line 10: why not to show also transpiration rate, or better stomatal conductance in the table? This help convincing the reader that stomata were closed at night. Photosynthesis alone is not sufficient to prove efficient stomatal closure at night. Pag. 19878 line 12: you mention that O<sub>3</sub> concentration at the inlet was kept constant at 60 ppb. Did you measure O<sub>3</sub> concentration outside the cuvette? It seems so, looking at the appendix. This may inform on the total O<sub>3</sub> flux inside the cuvette and may be directly related to stomatal and non-stomatal processes. Figure 2 would benefit of O<sub>3</sub> flux. In the appendix you show that O<sub>3</sub> flux was measured, so why not to include it? As it is, the figure show that some diterpenoids are fast consumed by O<sub>3</sub> supporting your thesis of relevant surface reactions, but the steady state of VOC suggests that surface reactions are important only in the first minutes and then what happens? Leaves stop removing O<sub>3</sub>? Or, perhaps, stomata keep sustaining O<sub>3</sub> removal when surface reactions are negligible? Pag. 19881 line 22: other papers after Laisk et al. show that O<sub>3</sub> may accumulate in the stomata especially under high O<sub>3</sub> concentration and low stomatal aperture, thus intercellular O<sub>3</sub> concentration may be above 0. If the O<sub>3</sub>-reactive bottom of stomata is not perfect O<sub>3</sub> scavenger, you may find that stomata are even less important, perhaps your model evaluation and discussion should consider this possibility. Pag. 19884 line 23: Fig. S1 support your finding that surface reactions occurs fast to the plant surface, but the reactive surfaces are fast depleted of diterpenoids. The surface contribution to O<sub>3</sub> removal is not continuous and this should be stressed in the text. Pag. 19885 line 19: Figure S3 shows that for several hours the O<sub>3</sub> conductance in stripped leaves stays high (but still decreasing). You assess in the text that the ozone protection last for long

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periods (1,5 days as it seems in the figure S2). However the cis-abenol signal does not seem to fully recover after the dark period in Fig. S2, suggesting that manipulation of leaves may have produced unrealistic emissions of cis-abenol. Moreover, spikes in MVK signals in Fig. S2 are not the same, suggesting that perhaps O3 concentration at the cuvette inlet were changed during the experiments? The dynamic of O3 at the cuvette outlet suggest that other factors influence the O3 flux in the cuvette. Please read my previous comments: the paper leave high uncertainty on the real O3 flux in the cuvette. Pag 19885 line 27 and pag. 19886: Please see my previous comment: Fig.4 is convincing if you can demonstrate that stomata did not play a role at night for all tobacco varieties. You do this showing negligible rates of water transpiration at night for all varieties. Since you measured E (shown in the appendix), why not to discuss this? Pag. 1988: the resistance scheme is clear, but the assumption that O3 is fully detoxified inside stomata may not be true.

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Interactive comment on Atmos. Chem. Phys. Discuss., 15, 19873, 2015.

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