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Atmospheric Chemistry and Physics
Discussions

Interactive comment on "Effect of atmospheric ageing on volatility and ROS of biodiesel exhaust nano-particles" *by* A. M. Pourkhesalian et al.

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Major comments:

Comment 1: Why was not any technique for chemical characterization used in this study? Information of chemical composition would be useful in order to understand potential toxic properties. Thermo-optical analysis of organic and elemental carbon would also have been useful to see whether the increased volatility comes from increased fraction of organic aerosol.

Response 1: It was previously established that ROS correlates well with the specific component of OC (see for example: Miljevic, B., Heringa, M. F., Keller, A., Meyer, N. K., Good, J., Lauber, A., et al. (2010). Oxidative Potential of Logwood and Pellet Burning

Particles Assessed by a Novel Profluorescent Nitroxide Probe. Environmental Science & Technology, 44(17), 6601–6607). Also, volatility is an indirect measure of potentially reactive OC [Stevanovic, S., Miljevic, B., Surawski, N. C., Fairfull-Smith, K. E., Bottle, S. E., Brown, R., and Ristovski, Z. D.: Influence of Oxygenated Organic Aerosols (OOAs) on the Oxidative Potential of Diesel and Biodiesel Particulate Matter, Environmental Science & Technology, 47, 7655-7662, 10.1021/es4007433, 2013]. Furthermore the focus of this manuscript was to show the effect of atmospheric aging on the semivolatile fraction and its contribution to ROS content. Aging will not increase the amount or percentage of elemental carbon and almost certainly it will increase the amount of OC as it increased volatility. The composition of OC will change and its effect was demonstrated here. Authors agree that a more detailed chemical analysis of gaseous and particulate phase may shed more light onto the underlying processes that are creating ROS. However, that was not the focus of this study and it is planned to be done in some of our future experimental investigations.

Comment 2: The R2-values should be given for the regressions lines in the figures. Comment 2: The R2-values were added for the regression lines in the captions of the corresponding figures.

Comment 3: The paper gives too little conclusive evidence that biodiesel aerosols might be more toxic and that the overall toxicity depends on the fuel. Only ROS-experiments have been performed. You should look at more toxicity endpoints before stating conclusions about overall toxicity.

Response 3: ROS is considered as a valuable tool to estimate the oxidative potential of aerosols (which is supported by numerous publications in the area). Moreover OP is considered to predict potential toxicity well (see for example: Møller, P., Jacobsen, N. R., Folkmann, J. K., Danielsen, P. H., Mikkelsen, L., Hemmingsen, J. G., et al. (2010). Role of oxidative damage in toxicity of particulates. Free Radical Research, 44(1), 1–46.). The statements given here were made based on the comparison on both the reported values between each other and in regards to petrol diesel that was a baseline fuel. ROS concentrations cannot be treated as the measure of the overall toxicity but particulate potential to create negative health effects- the term "potential toxicity" was used in the manuscript.

Comment 4: You should state a cumulative OH-exposure or a similar measure for you experiment, not just make an approximation of the atmospheric aging based on the literature.

Response 4: Authors agree with the reviewer. However, this was qualitative study of the effect of the aging. The sentence has been added to address this:" OH radical formation was not monitored and reported as this was a qualitative study showing the general effect without the quantification of SOA yields". -Line:124

Comment 5: In the abstract it is stated that the chemical composition of the exhaust changes upon aging, it is very likely, but since the chemical composition is not determined, this cannot be concluded.

Response 5: Total amount of volatile organics present on particles changes when new species were condensed on the PM or when the existing species were oxidised. In both cases, chemical composition of volatile fraction has to be changing. As none of the more detailed chemical analyses of the mentioned processes were conducted, the nature of the change was not specified or what were the underlying processes. Authors believe that based on this, it is still fair to say that chemical composition of the exhaust changes with the aging.

Comment 6: The engine itself EURO3 is rather old and it is also not clear whether there is any device for exhaust after treatment connected in your setup. Are the results relevant for the newer vehicles with exhaust after treatment that is used nowadays? I should be stated in the test that this might not be the case. Also have you tested your setup with other engines, do you see the same results?

Response 6: Technology is the same for EURO 3, 4 and 5. In contrast to EURO 4 and

5, EURO 3 does not have after-treatment devices connected to the exhaust pipe. As the study here was considering the dynamics of the raw exhaust, the overall aim was to study the phenomenon of aging and the subsequent changes; the use of EURO 3 is justified. In addition, the majority of trucks on Australian roads are still having EUR 3 engines.

Comment 7: The DustTrak measures scattered light from particles. The masses are only indirectly derived from light intensity. It is not correct to express these measurements as mass determinations. They are just relative in arbitrary units.

Response 7: The authors agree with the reviewer‘s comment. For that reason Dusttrak mass measurements were converted to gravimetric measurements according to a procedure described in a previous study [Jamriska, M.Diesel bus emissions measured in a tunnel study Environ. Sci. Technol. 2004, 38 (24) 6701– 6709]. This reference has been added to the manuscript. Lines:119

Comment 8: The shaded areas in figures 4, 6 and 8 needs to be explained in the caption.

Response 8: Authors agree with the reviewer. Captions were amended to include explanations.

Comment 9: I do not like acronyms in the title. I prefer that "ROS" is expressed Reactive Oxygen Species until it is explained in text. I am not sure that all the readers of ACPD immediately associate " ROS" with these types of species.

Response 9: Authors agree with the reviewer. The tile has been changed into: Effect of atmospheric ageing on volatility and reactive oxygen species of biodiesel exhaust nano-particles âĂČ

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/15/C5050/2015/acpd-15-C5050-2015-

supplement.pdf

Interactive comment on Atmos. Chem. Phys. Discuss., 15, 6481, 2015.

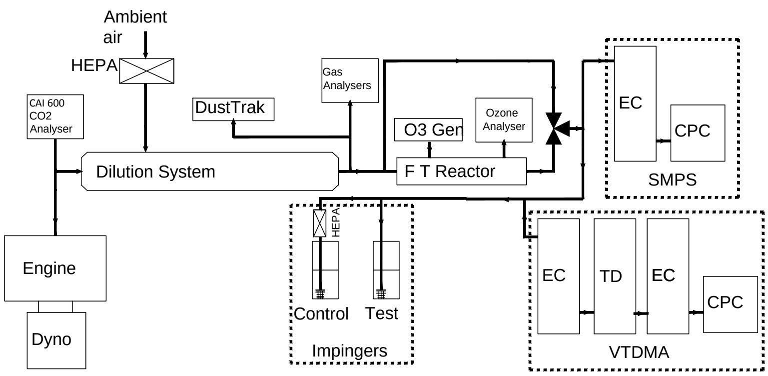

Fig. 1. Experiment setup HEPA: High-Efficiency Particulate Air Filter; F T reactor: Flow-Trough Reactor; O3 Gen: Ozone Generator; Ozone Analyser: EC9810 Ecotech; EC: Electrostatic Classifier; TD: Thermo-Denud

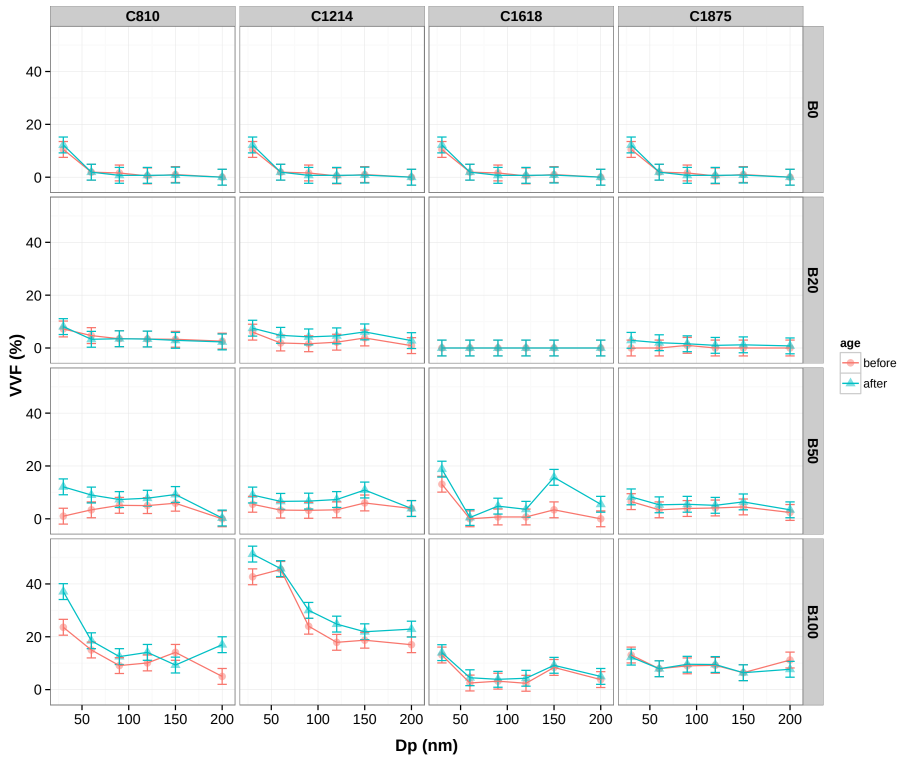

Fig. 2. the volumetric volatile fraction (vvf) of particles versus particle pre-selection sizes for different biodiesels and different blends before and after aging. Each column is dedicated to one of the bio

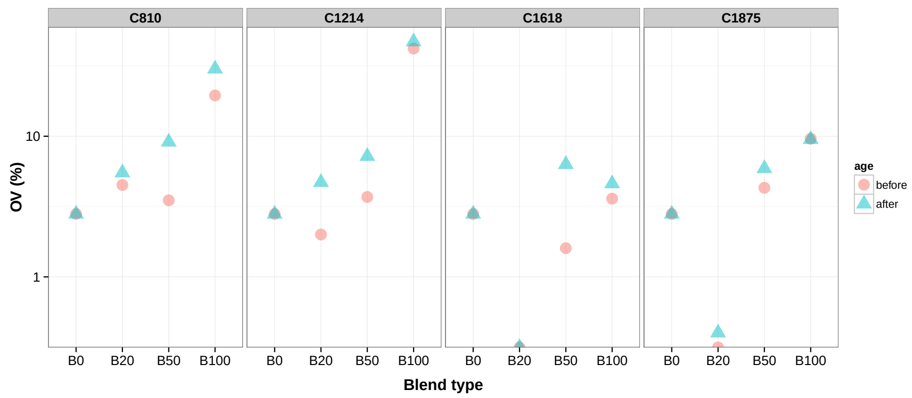

Fig. 3. volatility of particulate matter versus different blends for petro-diesel and tested biodiesels before and after aging in the flow through reactor. Blue points are due to aged particulate matter and r

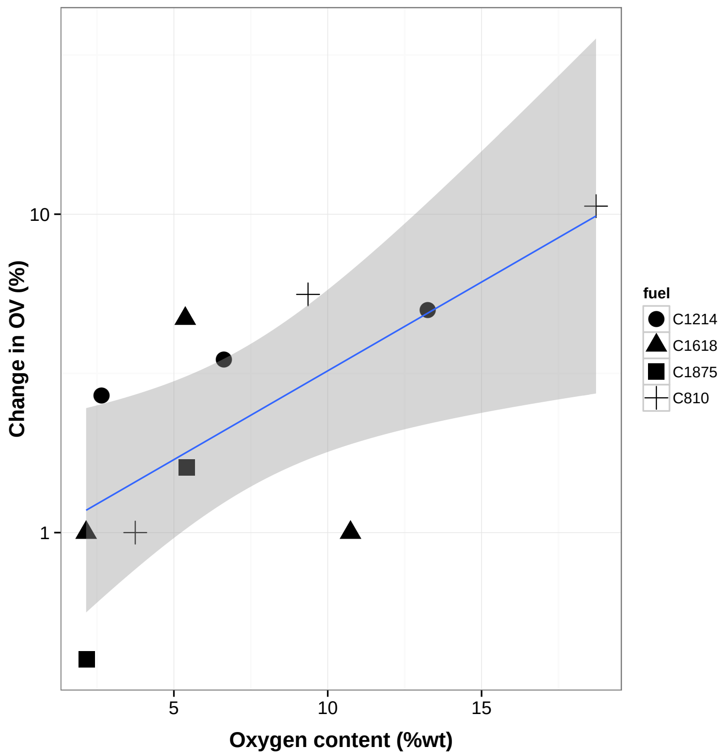

Fig. 4. change in volatility of particles before and after aging against oxygen content of the blends. Different blends are shown with colours and different shapes as can be seen in the legend show different

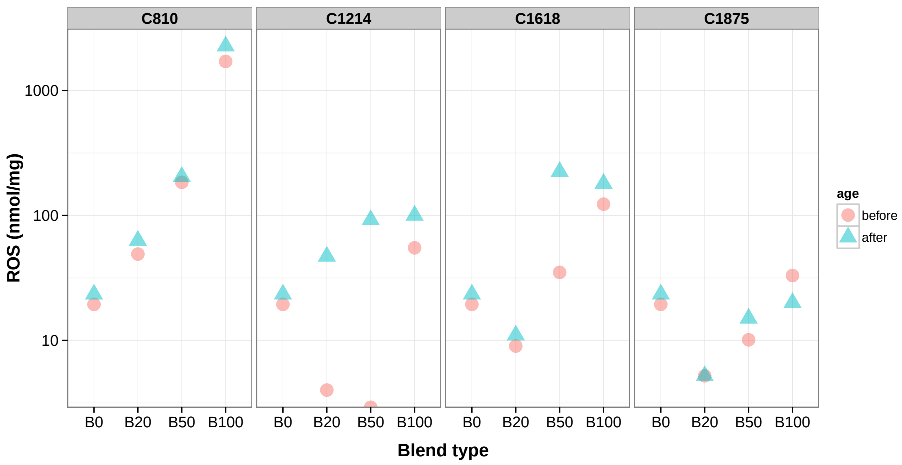

Fig. 5. ROS levels of particulate matter versus different blends for petro-diesel and tested biodiesels before aging (red circles) and after aging (blue triangles). Different tested biodiesels can be seen at

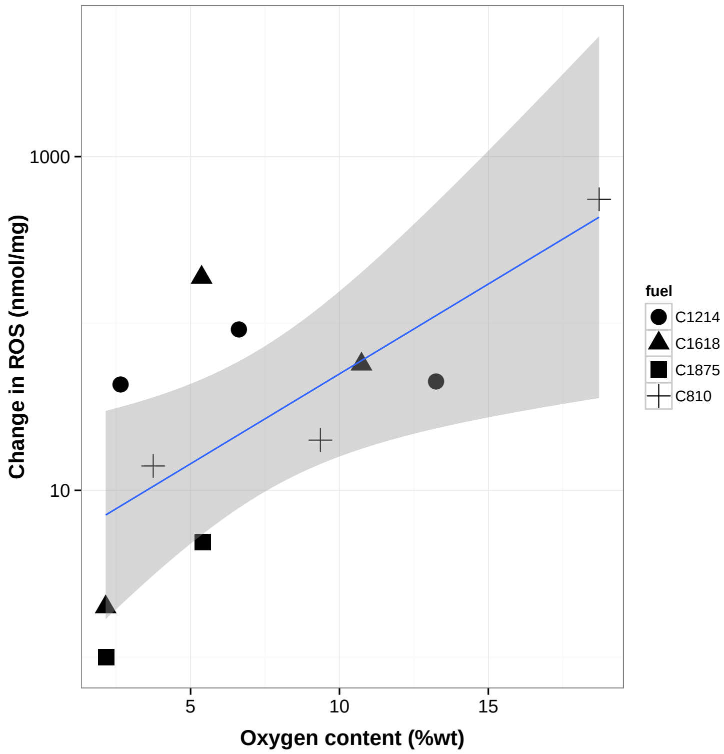

Fig. 6. the correlation between the change in ROS levels and oxygen content the fuels before and after aging . The point corresponding to C1875 is excluded from the model. The grey area shows the 95% confiden

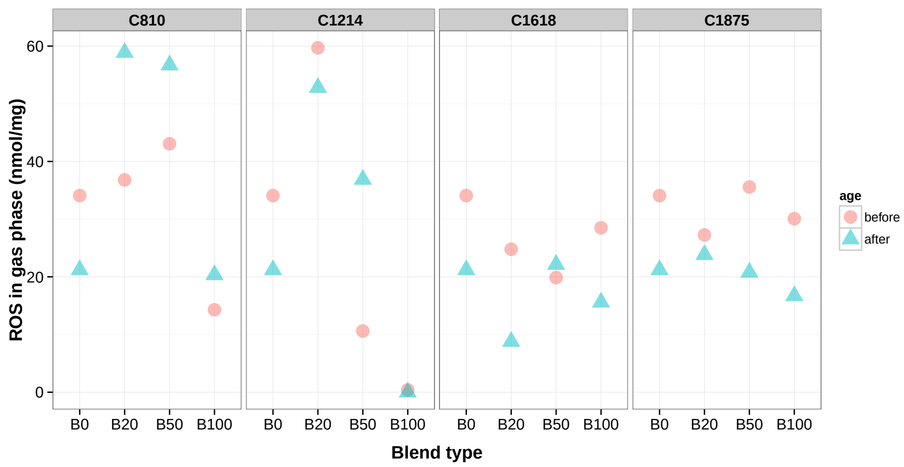

Fig. 7. ROS levels in gas phase before and after aging. Fresh and aged particulate matter are separated using blue color for aged PM and red for fresh PM.

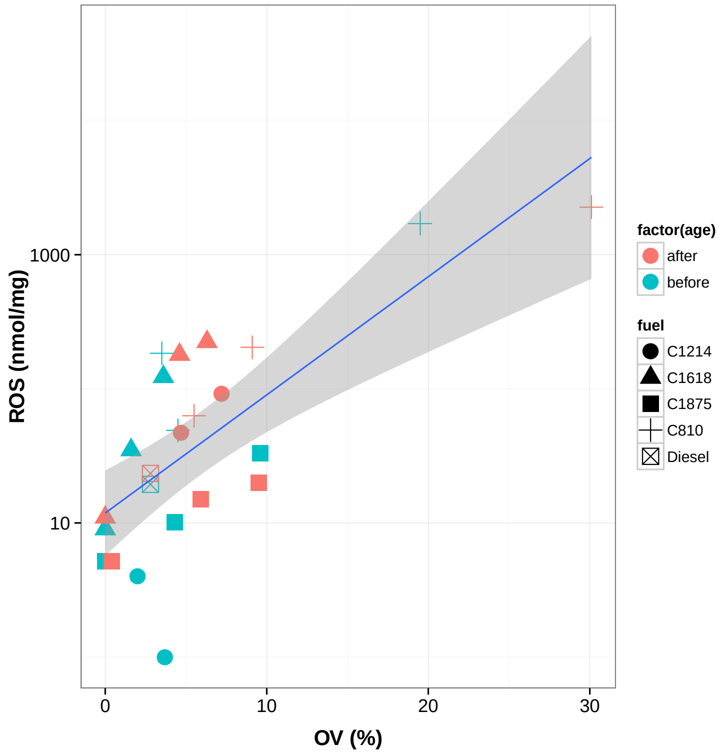

Fig. 8. the correlation between ROS of particulate matter and the volatility of particulate matter. Fresh and aged particulate matter are separated using blue color for fresh PM and red for aged PM, also the