

***Interactive comment on* “Emission of sunscreen salicylic esters from desert vegetation and their contribution to aerosol formation” by S. N. Matsunaga et al.**

S. N. Matsunaga et al.

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Special major comments:

13620, line 19: "... the salicylic esters are predicted to be effective precursors ..." As far as I understand this is assumed or deduced from sesquiterpenes but there is no evidence given that this is true

— We have modified this sentence to indicate that this is assumed to be the case. We have modified other sections of the manuscript to indicate that this is a potential contribution that needs to be verified. We believe it is a reasonable assumption since even the oxidation products of monoterpene, which is C10 hydrocarbon, can be an aerosol component, effectively (Kavouras et al., 1999). The oxidation products are assumed

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to be oxygenated compounds such as carbonyl, carboxylic acid and/or multifunctional compound. Those are less volatile enough to be condensed onto the aerosol phase. The esters are C15 and C16 compounds, therefore, it is easily assumed that the oxidation products tend to have larger molecule and be less volatile than oxidation products of monoterpene.

13623/24, Experiment: The experiment is not clearly enough described. How many samplings were done per plant? If only one per plant (as I assume) this might not be representative for the whole plant. Were the experiments also done under different conditions, particularly under different temperatures?

— We have added additional details to the description in section 2.1 Experiment. The SQT sample collection needs 2-4 hours and the cuvette collected only one sample for each plant. However, SQT was also collected using a larger enclosure bag without temperature control. So there are two measurements for some plants. All of the samples from the larger bag showed same compounds as from samples from the cuvette although the emission rate were much larger in most case due to a high temperature of the bag inside.

Figure 1 and the description in section 2.1 are difficult to understand. If there is an inflow of 720 ml/hr and an outflow of 220 ml/min plus 300 ml/min: what about the rest? Were the volumes measured and their fluctuations considered in the evaluation?

— The inflow is 720 ml min⁻¹, and GC/FID analysis and SQT collection requires 520 ml min⁻¹ in total. The remaining 200 ml min⁻¹ is over flow from the cuvette providing a positive pressure to isolate the inside air of the cuvette from the ambient air. The flow rate was controlled during the collection, so the fluctuation is negligible compared to the analytical error derived from the concentration process.

In line 13/14 I cannot distinguish between the VOC analysis (at 220 ml/min) and the analysis of "another portion of air" (how much???) by taking samples and subsequent analysis by GC/FID. Which VOCs have been additionally analysed. What were the

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results?

— There was no another portion and this sentence has been changed to correct this description. The GC/FID analysis was for isoprene and monoterpenes. The results for those are described in another paper by Maria Papiez et al that is currently under review.

The extracts were concentrated to less than 2-3 microliters. This seems to be a very small volume. What are the implications, particularly with respect to possible losses during the concentration process?

— The extract was concentrated to the smallest volume visible as a liquid. This volume is 2-3 micro liters. Because 30 micro liters of solvent (hexane) is added into this final extract, error on the final volume (2-3 micro liters) is negligible. Loss of the compounds during the concentration process is large (55%), however, this loss factor is relatively stable (10-15% varies) and was considered when the emission rates were calculated. Some additional description of this procedure has been added to the end of section 2.1 Sample collection and treatment.

A description of the QA/QC activities and the overall uncertainty is almost completely missing. How did the retention time vary? What about recovery rates of the used internal standards? I do not understand how the "loss factor" was determined and what the uncertainty of this factor is. What is meant by "the uncertainty due to the concentration process could be standard deviation of 10 - 15 %"?

— The text has been modified to expand and clarify this QA/QC and uncertainty descriptions. Retention time was checked using a solution of the authentic standards every day. In addition, the location where peaks for the salicylic ester appear does not show any other major peaks.

— The compounds were quantified with a comparison of the peak area between the sample and external standard.

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— The loss factor is determined by comparison of the concentration between concentrated and non-concentrated (prepared only by dilution of solution).

— When same standard samples were concentrated, they showed a 10-15% of standard deviation.

Figure 1 indicates that the sample was taken at 220 ml/min, but that another line goes to GC/FID. I understand in the text that the sample was analysed later by GC/FID. What is correct?

— Another line is for a measurement for isoprene and monoterpene in situ. The SQT samples were analyzed with a GC/FID in the laboratory.

Figure 2: Are these mass spectra of the standards or of the samples? How do the spectra of standards and samples compare?

— The mass spec in the figure is from a sample. This analytical technique allows us to have 30 µl of extract for injection. Because one analysis needs only 1-2 µl (1 for GC/MS, 2 for GC/FID) of the extract, one sample can be analyzed several times. The mass spec of the sample and authentic standard were compared for each compound and showed the same spectra. GC retention time for the compound was also compared between sample and standard and showed an agreement. A sentence: The mass spectra and GC retention time of the GC peaks of the standard and sample showed a good agreement; has been added into the 2.2 Analysis part.

13625, Emission model: What about the land cover inputs? Does this refer to the desert plants under investigation or to the land cover of the whole Earth? What is the role of Maria Papiez? If she contributed to the paper she should be co-author. Otherwise she should be acknowledged or cited.

— We have expanded and clarified the text in this section to indicate that landcover data from a companion study (now referenced in the text) was combined with the existing

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MEGAN landcover.

13625, equation 1: How can you be sure that the equation is valid for the esters? It has been measured for sesquiterpenes and it is not clear whether the physico-chemical properties of them are comparable. The emission factors in Table 1 strongly depend on this equation. Why has the temperature dependence not been measured instead of making this assumption?

— This section has been removed from the manuscript. Instead we now compare monoterpene and sesquiterpene emissions at the average temperature measured during this study.

13625, line 24: It should be said that T is given in K in equation 1, because degrees C are used in the rest of the paper.

— This section has been removed from the manuscript. Instead we now compare monoterpene and sesquiterpene emissions at the average temperature measured during this study.

13626, section 3.2: The application of the model for this particular case needs to be described. How long was the simulation, which temperatures were prevalent? Which was the SOA yield? How big is the uncertainty of this number? It is verified to take the SOA yields from SQT? How large are the absolute emissions? How do they compare to other BVOC emissions from other species at other places (in the US)? Which BVOC emissions by these plants exist and may be of importance and how have been taken into account? These are questions that need to be answered before reader can judge how important these emissions are in the context that has described in the introduction ("impact on regional air quality and global climate").

— The text has been modified to improve the description of the model application and to clarify that it is simply a preliminary exercise to determine if there is any possibility that these emissions could be important. The magnitude of the monoterpene and

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sesquiterpene emissions in this region is discussed in a companion paper.

13626, Conclusions line 23: As far as I understand its just a hypothesis that they important for SOA formation, the SOA yield has not been shown nor has it been sufficiently clear that there is good reason to take the SQT SOA yield. Additionally, may be only important in deserts (whrere no other BVOC emission exist). This be made more clear.

— The text has been modified to indicate that this study only shows that these emission could be important and that additional studies are needed to determine the importance.

Fig. 3: I am missing some geographical information like coordinates or scale. Additional information on the time/averaging period etc. would be helpful. In the text, said that the salicylic esters contribute at least 25 % to the total BVOC SOA in regions. This Figure indicates that most regions are between 6 and 18 %.

— The figure has been modified so that it now shows the relative contribution to emissions at 32 C and not SOA. A scale has been added.

Minor comments: 13620, line 13: explain the unit dwg 13620, line 23/25: What is the difference between Las Vegas area and Las Vegas region? 13626, section 3.2: It is Fig. 3 (not 2).

— The dwg means dry weight gram. An explanation has been added. — Las Vegas region has been changed to Las Vegas area. — The figure number has been corrected.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 13619, 2008.

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