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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Volatile organic compounds (VOCs) in photochemically aged air from the Eastern and Western Mediterranean" *by* Bettina Derstroff et al.

Bettina Derstroff et al.

bettina.derstroff@mpic.de

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Response to Reviewers comments. We would like to thank the reviewers for their time and comments. We believe the changes we have made in response to the specific points raised have improved the paper. We also thank both reviewers for noting the value of our dataset to studies in the region and the atmospheric community. However, we were disappointed that we did not communicate effectively the "new and important information" contained in the paper to reviewer 1 and that reviewer 2 labelled the work "a data description report". We respectfully point out that our paper presents a comprehensive dataset from an interesting new location which permits airmass contrasts from eastern and western Europe. It also includes state of the art trajectory modelling anal-

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ysis innovatively coupled with measurements to empirically assess marine deposition rates for the first time for selected OVOC , a comparison to a chemical modelling analysis for the site and comparisons to earlier regional measurements to address decadal changes. As such we do believe the paper does contain new information relevant of the readers of Atmospheric Chemistry and Physics and hope that with the revised version, including the suggestions of the reviewers, the value of the paper will become clearer. Our response to the specific points raised are given below after the reviewer's remarks (in italics). Reviewer comments:

Referee 2 1. Ln 71 Should add recent Muller et al paper (Nature Comm) to discussion of methanol budget.

Thank you for this suggestion. The text was altered as follows:

"Methanol is primarily emitted from plants (Galbally and Kirstine, 2002), with a relatively small photochemical production term in the estimated global budget, 37 Tg yr-1 from a total of 242 Tg yr-1 found by Millet et al. (2008). However, recent model calculations by Müller et al. (2016) revealed that the photochemical reaction between methyl peroxy and hydroxyl radicals is, depending on the region, a significant source for methanol. The reaction was found to result in 115 Tg yr-1 of methanol, which is in the range of the global terrestrial emissions. For example Millet et al. (2008) list a methanol source from terrestrial plant growth of 80 yr-1 and from plant decay of 23 yr-1. One of the main sinks of methanol is the oxidation by OH, while the role of the ocean is not completely characterized: Millet et al. (2008) report a methanol sink via OH oxidation of 88 Tg yr-1 and an ocean uptake of 101 Tg yr-1 of a total sink of 242 Tg yr-1. In contrast, Jacob et al. (2005) found a loss of methanol via the reaction with OH of 129 Tg yr-1 while the ocean uptake amounts only to 10 Tg yr-1 from a total sink of 206 Tg yr-1."

2. Ln 155. Would like more information on the large variation in the lab calibrations. Do the authors have any hypotheses for the challenges? Beyond adding uncertainty to the data, does the potential for RH dependent error alter any of the conclusions derived

from these data?

Literature confirms that the calibration of the PTR-TOF-MS for acetic acid represents a challenge: Warneke et al. (2001) found no humidity dependency, Feilberg et al. (2010) report a linear relation while Haase et al. (2012) state that the behavior strongly depends on the instrument itself. In our case the calibration performed after the campaign in the laboratory is likely the more reliable, because the calibrations were performed at more humidity levels and using more calibration steps than in the field. Still, this calibration in the laboratory was done after the instrument was transported so that we cannot exclude that the sensitivity has changed. Therefore an averaged value with a high error was assumed. In the field as well as in the laboratory it was found that the sensitivity decreases with increasing humidity. Therefore the overall trend in the data is correct.

3. Please explain how the solubilities are determined for use in the models. For several compounds, these are pH sensitive (H*)?

The reviewer has made essentially the same point as raised by Dr Taraborrelli (see answer), namely that the H* values rather than Henry Law constants should be used. This is quite correct. In fact the version of the EMAC model we used did apply the pH dependent H* approach. By comparing the EMAC results to those produced before the introduction of H* into the model we see negligible differences in the dry deposition velocities which implies that the removal rate is limited by the aerodynamic and quasi-laminar boundary layer resistances and not the H*-inclusive surface resistance terms (see details in Kerkweg et al. (2006)). In order to investigate this effect further, we now amend scenario 3 in our model simulations to be a sensitivity test of the H* terms and we systematically vary the EMAC determined deposition velocities to determine the sensitivity of the mixing ratios to these values.

4. Ln 270. This PP is confusing as earlier there is a discussion of what the ecology of the island is.

We have amended the text to make this point more clear. The inserted text reads:

“This emission behavior of the monoterpenes indicates a domination of a light dependent emission regulation which is typical for vegetation without VOC reservoirs. Hence, coniferous tree species with resin ducts or herbal plants with glands may play a minor role here. However, an emission classification of all the tree species found at the site is not available. Furthermore, we must take into account that VOC emissions from plant species with a temperature dependent release from storage pools may also show some degree of light dependency (Staudt et al., 1997; Owen et al., 2002).” References Staudt, M., Bertin, N., Hansen, U., Seufert, G., Ciccioli, P., Foster, P., Frenzel, B., Fugit, J.L., (1997) Atmospheric Environment Vol. 31, No. SI, pp. 145-156. Owen, S.M., Harley, P., Guenther, A., Hewitt, C.N. (2002) Light dependency of VOC emissions from selected Mediterranean plant species. Atmospheric Environment 36, 3147–3159.

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