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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.

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Response to Reviewers comments. We would like to thank the reviewers for their time and helpful 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 uniquely permits airmass contrasts from eastern and western Europe. It also includes state of the art trajectory

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modelling analysis 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 to assess dominating processes, and comparisons to earlier measurements to address long term regional 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 this paper to our community will become clearer. Our response to the specific points raised are given below after the reviewer's remarks. Reviewer comments:

Referee 1

Several concerns and specific suggestions of the paper are: 1. Local anthropogenic emissions: for a population of 1.15 million, it might be worth to explore the importance of local emissions on the VOC levels. Could the high correlations of VOC vs CO (and aromatics) give some insights?

The location of this campaign was carefully chosen to be close to the upwind west coast of Cyprus (<10km from the sea), and on a remote hilltop, in a sparsely populated area to minimize local anthropogenic influence. The prevailing winds advected airmasses from the west (Western Europe) and north (Eastern Europe) over several hundred kilometers of sea and then over the short stretch of land between coast and site. The nearest conurbation was the small village of Polis, which is located to the northeast of the site with only 1975 inhabitants and negligible influence on our data. Although the island of Cyprus does have over 1 million inhabitants they do not influence our data, rather our data represent the photochemically processed air from Eastern and Western Europe. We add the following sentence to make this clearer in the text. "Although Cyprus has a population of over 1 million their emissions do not influence this dataset since no Cypriot cities or industries lie upwind of the site. Instead the measurements analyzed here represent the transported and photochemical processed pollution emerging from Eastern and Western Europe."

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2. The title doesn't reflect what is told from the manuscript. It stated 'photochemically aged air' but the manuscript doesn't provide any analysis on this matter.

We are somewhat confused by this comment. As our introduction clearly states our campaign location was carefully chosen to be in a position to measure photochemically processed air emerging from Eastern and Western Europe. This is in contrast to the majority of atmospheric chemistry campaigns which tend to be positioned close to a source (e.g. in a megacity or a forest). The FLEXPART model which we have used extensively in this study (see for example figures 1,8,13) shows transport times from the continental emission sources which are a minimum of 12 hours from Eastern Europe and a minimum of 2 days from Western Europe. During this time the air was photochemically processed (by OH and photolysis from the intense Mediteranean sunlight.) The extremely low NOx values measured during the campaign are also indicative of very aged air. We therefore think that the title does reflect exactly the reality of the campaign and choose to retain it. However, in order to make this point clearer we have amended the abstract to read "The Lagrangian model FLEXPART was used to determine transport patterns and photochemical processing times (between 12 hours and several days) of air masses originating from source regions in Eastern and Western Europe." In addition we now add to the introduction the following sentences, "This campaign was designed to investigate the chemical characteristics of polluted air emerging from the European continent which is then photochemically processed over the Mediterranean Sea between 12 hours and several days en-route to the island of Cyprus. It is therefore in contrast with most atmospheric chemistry campaigns that generally investigate source impacted locations (e.g. in forests and megacities)."

3. Abstract: loss rates: significant digits should be consistent for all reported numbers. These numbers all seem very small. Are they important?

The reviewer is correct to question this formatting, thanks. The numbers in the abstract are now consistently given in pptv for clarity and the significant digits are adapted thus: . . . " the marine boundary layer (MBL) with loss rates of 105$\pm$11 pptv/h, 59$\pm$7 pptv/h,

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54±8 pptv/h from Eastern Europe and 59±9 pptv/h, 19±4 pptv/h and 29±4 pptv/h from Western Europe"

4. Introduction (and its references) should be updated to reflect some newest developments on their global budgets particularly for methanol and acetone. More regional studies for this area should be cited otherwise I don't really see the motivations of this study. At the time of submission we thought we had faithfully accredited all relevant published previous work. While reviewer 1 does not give any information on overlooked references, we are grateful to reviewer 2 to pointing out the Müller et al reference which was published shortly after our last literature review. We have also since found a new relevant reference Khan et al. (2015) concerning the global budget of acetone. Both these references are now included in the text discussion.

"According to Fischer et al. (2012) the global acetone budget sums up to 146 Tg/yr, 32 Tg/yr being terrestrial emissions from biosphere and 31 Tg/yr being photochemical production (26 Tg/yr anthropogenic,5 Tg/yr biogenic). Khan et al. (2015) state a global acetone source of 72.7 Tg/yr. The main acetone sinks are photolysis and reaction with OH: Fischer et al. (2012) report a loss of 33 Tg/yr by OH oxidation and 19 Tg/yr by photolysis from a total sink of 146 Tg/yr. Depending on the season and geographical location the ocean can either be a sink (82 Tg/yr) or a source (80 Tg/yr) of acetone (Fischer et al., 2012). Khan et al. (2015) on the other hand state a global acetone source of 72.7 Tg/yr, of which 55.6 Tg/yr are photochemical production and 17.1 Tg/yr direct emission. From the total sink of 72.9 Tg/yr 30.8 Tg/yr represent OH oxidation, 30.3 Tg/yr photolysis and 11.8 Tg/yr dry deposition and the ocean is regarded as being globally in a near equilibrium state (Khan et al., 2015). A global acetone source of 95 Tg/yr is given by Jacob et al. (2002). The main contributions are emissions by terrestrial vegetation (33 Tg/yr), by the ocean (27 Tg/yr) and the oxidation of isoalkanes. Jacob et al. (2002) determined a sink by OH reaction of 27 Tg/yr and by photolysis of 46 Tg/yr from a total loss of 95 Tg/yr."

And for methanol "Methanol is primarily emitted from plants (Galbally and Kirstine,

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2002), with a relatively small photochemical production term in the estimated global budget, 37 Tg/yr from a total of 242 Tg/yr 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 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 Tg/yr and from plant decay of 23 Tg/yr. 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 and an ocean uptake of 101 Tg yr-1 of a total sink of 242 Tg/yr. In contrast, Jacob et al. (2005) found a loss of methanol via the reaction with OH of 129 Tg/yr while the ocean uptake amounts only to 10 Tg/yr from a total sink of 206 Tg/yr."

Regarding the last sentence in this comment "More regional studies for this area should be cited otherwise I don't really see the motivations of this study." We are again somewhat confused by this comment. Does the reviewer really mean to say that in his/her opinion measurements are only worth doing in regions where measurements already exist? The measurements we present here are new, taken in an interesting location downwind of the European continent where the air from two distinct locations is extensively photochemically processed prior to measurement. Where available we do compare with previous regional studies conducted in the Mediterranean marine boundary layer (e.g. measurement made on Crete) in order to deduce longer term trends but what we present here is a brand new comprehensive dataset that is analyzed to develop new perspectives on the atmospheric chemical processing of OVOC.

5. Humidity dependent instrument sensitivity: a. Only two calibrations were performed: beginning and end of the campaign, but the humidity seems to vary a lot during the campaign. It is unclear how humidity was accounted for the measurements. Given some conclusions are related to the variability of ambient humidity, authors should be

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very careful on their observation's dependence on RH. b. The paper also commented that instrument sensitivity for methanol and isoprene didn't show any humidity dependency. Why is that? It seems PTR methanol sensitivity has a strong dependence on RH. c. One simple check on the RH effect is to examine if the background signal changed a lot during the campaign.

a) The reviewer is correct to address the humidity dependence of the calibrations given the strong variations of RH experienced during the campaign. "The PTR-TOF-MS was calibrated at 4 mixing ratios (spanning the measured range of compounds) and at 3-4 humidity levels (between approximately 25%-80% humidity) both before and after the campaign using a 14 component commercial gas standard (Apel Riemer Environmental). Great care was taken to account for this humidity dependence in each datapoint. The sensitivity of the instrument for each individual data point was derived from a linear interpolation over time between the two calibrations and corrected for the co-measured ambient relative humidity at that time. Sensitivity changes between the two calibrations (2.5 weeks apart) were generally modest, ranging from 0.6 ncps /ppbv (e.g. isoprene) to 3 ncps /ppbv (e.g. methanol)."

The above text is now added to the manuscript to clarify how the measurements were quantified. More specific information about the humidity dependency of acetic acid can be found under comment 2 of referee 2.

b) Most compounds measured by PTR-TOF-MS show a strong humidity dependence between 0 and 15% (whereby dry conditions are most sensitive), but with increasing humidity the dependency weakens so that decreases in sensitivity between 70 and 80% humidity are very small. This behavior was observed for all compounds except isoprene and methanol. Isoprene shows almost no humidity dependency, because its reaction rates with the primary ion and the water cluster have roughly the same value as has been previously reported by Smith et al., 2001. The variations in the sensitivity for methanol did not show the same characteristic exponential behavior described above (see answer a), so that no interpolation was made. However, since the values

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varied by only 10-20 %, an averaged calibration factor was used instead. The underlying reason for this anomalous behavior is not known in the case of methanol. However, it was noted that the sensitivity of the instrument shows a higher variability in the lowest humidity range. For very short periods during the campaign the ambient humidity was below the lower limit of the calibrated humidity range yet the absence of a trend for methanol precluded interpolation. Previous measurements in our laboratory have shown a variation in the sensitivity for methanol of 35% within the humidity range 0 and 25 %. Therefore a conservative maximum error of 35% was assumed for methanol."

The above text is now inserted in the revised manuscript.

c) Background variations experienced during the campaign were small and unsuitable for judging humidity dependences. It should be noted though that the background varies not just as a function of humidity but also with instrument noise. Therefore humidity dependent calibrations are the best way to determine this dependency (as we have done). For our quantification we subtract the background corresponding to the measurement time interpolated between background measurements, then apply our humidity dependent calibration factors for each data point (see above).

We believe the text inserted in answer to points a) and b) should make the calibration procedure clearer.

6. Page 6. Acetic acid measurements: It seems PAA measurements were not subtracted from the PTR 61.0284 amu. Would the main conclusion change if such subtraction were attempted?

A fraction of the PAA data was not subtracted from the 61.0284 signal because the PAA signal was only measurable during a small portion of the campaign with very low counts-per-second (ca. 0.3). It's inclusion would therefore not affect the conclusions. This point was already made in the text, but the text has been amended for clarity in light of the comment, as below.

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“The PTR-TOF-MS was not calibrated for PAA and only detected it with low count rates (ca. 0.3 cps) at mass 77.0233 amu for a few days of the campaign. ŠpanËĞel et al. (2003) reported that 90% of protonated PAA can be measured at the exact mass of acetic acid, while 10% are recorded at the mass of the mother ion (77.0233 amu). Therefore PAA is not likely to have significantly influenced the acetic acid dataset for this campaign because of the low count rates.”

7. Section 2.2.2: So I assume the GC-MS reports speciated monoterpene measurments? Has any attempt done to compare the GC-MS measured vs. PTR measured C2 monoterpene? Are they consistent? Also, more details should be reported for the GC-MS system. And 8. Page 8 Line 253: again here it seems the PTR monoterpene is reported, but later GC-MS data is reported. It is very confusing which dataset is used for the monoterpene analysis.

The reviewer has suggested comparing the speciated monoterpene results provided by the GC-MS and the total monoterpenes measured by the PTR-TOF-MS. Therefore we now provide this information as described below. Firstly, the relevant information concerning the GC-MS system is added to the experimental section:

“Isoprene and monoterpenes (ïĄą-pinene, ïĄć-pinene , ïĄĎ-3 carene and limonene) were quantified by a commercial GC-MS system (MSD 5973; Agilent Technologies GmbH) combined with an air sampler and a thermal desorption unit (Markes International GmbH). The sample interval was 45 min while calibrations were carried out every 8-12 samples with a commercial gas standard mixture (National Physical Laboratory, UK). The detection limit was ≈1-10 pptv and the total uncertainty 20-30%. The volatiles were trapped at 30 °C on a low-dead-volume quartz cold trap (U-T15ATA; Markes International GmbH), which was packed with two bed sorbent (Tenax TA and Carbograph I). The trap was then heated to 320 °C and the compounds were transferred to a 30m GC column (DB-624, 0.25mm I.D., 1.4ïĄm film; J&W Scientific). The temperature of the GC oven was programmed to stay stable at 40°C for 5min, thereafter increase to 140 °C with a rate of 5 C/min and finally the rate was increased to 40 °C/min to reach the

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final temperature of 230 °C, which was held for 3 min. Due to co-elution of ïĄć-pinene and ïĄĎ-3 carene, a separation was not possible and therefore the signal was treated as the sum of the two species."

A comparison between the GC-MS and the PTR-TOF-MS data has now been added to the paper and it was made clear which data were reported in each case: the following text was added,

"Isoprene and several different monoterpenes were also measured by a GC-MS system operating at a lower time resolution at the same site. A comparison between the results of the two instruments can be found in the figure below. The two isoprene data sets are reasonably consistent with the PTR-TOF-MS system recording slightly higher absolute values in some parts of the campaign. A correlation of the two datasets resulted in a rˆ2 value of 0.86. The lower panel of the figure shows the data of ïĄą-pinene, the sum of ïĄć-pinene and ïĄĎ-carene as well as limonene measured by the GC-MS system. It is clear that ïĄą -pinene is the dominant species among the monoterpenes quantified, which lends credence to the PTR-TOF-MS data since the total monoterpene signal was calibrated with ïĄą -pinene. The sum of the monoterpenes measured by GC-MS are compared to the total monoterpene signal measured by PTR-TOF-MS at 137.13 amu in the upper panel. The PTR-TOF-MS data are higher than the GC data which was expected, because the sum on mass 137 amu can also contain monoterpenes other than those quantified by the GC-MS. The correlation coefficient between the two signals is (rˆ2=0.71) which is reasonable given the known differences in sensitivity, time resolution and unmeasured monoterpenes by GCMS. Generally, we have preferred to display and analyze the PTR-TOF-MS data in view of the higher data resolution and we now state which dataset is used explicitly as exemplified in the text below. "Figure 3 displays the campaign averaged, diel cycles of the sum of the monoterpenes and of isoprene measured by the PTR-TOF-MS instrument."

(see reply figures 1 and 2)

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9. Page 8 line 254: Any particular reasons that the tropical forest region is used to compare the data in Cyprus? The location of the site is 34 degree N, which is at mid-latitude.

The reason we compared the levels of isoprene and monoterpenes to the tropical forest is to set the current Mediterranean vegetation emission of isoprene and monoterpenes in a wider global vegetation context before making the comparison to previous regional measurements. In order to make this clearer we now amend the text to include a more northerly Boreal forest measurement campaign. We have amended the text as follows "This is in contrast to tropical forest regions where typical values of 7.6 ppbv isoprene and 1 ppbv monoterpene have been reported recently (Yañez Serrano et al., 2015) and Boreal forest regions where levels of isoprene and monoterpenes are ca. 100 pptv and 300 pptv respectively (Yassaa et al. 2012). Our results are consistent with levels reported previously from Mediterranean areas (Liakakou et al., 2007; Davison et al., 2009)."

10. Section 3.1: I would suggest the authors also take a look at MVK+MACR, since their lifetime is longer than isoprene so they could give a relatively regional perspective on the biogenic emission for Cyprus.

We are happy to follow the reviewer's suggestion to add data for the isoprene photo-product mass. This is now done in Figure 3. However, it should be noted that this reflects only the emission of isoprene and photooxidation in the circa 10 km of land between sea and the site. It does not give a representative regional perspective on the biogenic emission for Cyprus because of the short fetch of land between the coast and site (see answer to point 1).

(see reply fig 3)

We now add the following text to accompany this figure.

"Figure 3 also shows the diel cycle of the oxidation products of isoprene which are

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measured at mass 71.0491 amu and include methacrolein, methyl vinyl ketone and isoprene peroxides. The mixing ratio at this mass is lower than isoprene and offset in time so that it peaks at later values than the isoprene which is consistent with it being a photochemical product of the local emissions."

11. Page 9 lines 280-295: discussion on Fig.5. How does RH change your results? How does RH impact the observations here? It is stated that "But as soon as the wind came from a region where the distance between ocean and site was shorter, isoprene levels decreased rapidly", which is awkward written and need to be improved by the way. However, from Fig.5., it seems the opposite. Isoprene level is clearly higher after _9:30AM than before it, so does DMS.

As explained at length in response to point 5, great care has been taken in this dataset to account for changes in instrument sensitivity related to relative humidity. Each point is individually corrected for the humidity dependence and isoprene exhibited no humidity dependence for the reasons given previously. The intention in this section was to explain the morning peak in isoprene that occasionally occurred and which is exemplified in Figure 5. The text was changed as follows:

"Prior to the change in wind direction, the isoprene mixing ratio began increasing with temperature as expected. However, as soon as the local sea breeze set-in and the wind direction changed abruptly to the west, the isoprene levels decreased sharply. The apparent peak in isoprene is therefore generated by the wind change combined with the shorter section of isoprene emitting vegetated land between the site and the coast when the wind is from the west"

12. Page 10 line 335-337: 'the measured production. . . the loss rate . . .' I don't think they are ever mentioned in the method part. Are they measured or calculated?

We agree that our description of the rate of change of mixing ratio can be confused with flux measurements which were not performed here. We therefore amend the text for clarity to read as follows:

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"To investigate this further the median diel cycle of acetic acid was calculated for the period from the 16 to the 21 July. Between 6 AM and 2 PM the acetic acid mixing ratios increased by 0.77 ppbv $\pm$ 0.36 ppbv, so that the rate of increase in the measured ambient data was 0.10 ppbv $\pm$ 0.05 ppbv/h. Between 2 PM and 10 PM the levels decreased by 0.65 ppbv, which gives a rate of decrease of 0.08 ppbv $\pm$ 0.04 ppbv/h."

13. Page 11 Line 344-346: a) the authors state that secondary production is expected to be minor in a remote site due to a lack of precursors. However, this is only true if the sample is fresh. Are there any evidence suggesting the air is mostly fresh? Use some photochemical clocks could easily tell that (Isoprene/MVK+MACR, Benzene/Toluene, etc) b) I don't see evidence to support the conclusion that in-mixing from free troposphere contributed to the enhancement of acetic acid. It seems to be purely speculation here.

a) In this section the local diel cycle of acetic acid was investigated. Since the site was in a remote location at a short distance from the coast and the wind was mainly coming from the sea, we concluded that not enough reactive precursors were left to produce acetic acid locally. The reviewer correctly states that secondary production is less important at the point of emission ("fresh emission"), but it is also the case after considerable photo-oxidation has occurred (as in this case), as the rate of secondary production also declines as the emitted reactive emissions are oxidized to less reactive species. As the title states, here we investigate photochemically aged air where there is little reactivity left. To make that more clear the wording was changed to "local secondary production". Secondary production that took place during transport would influence the long term patterns of the acid, but not the diel cycle. This production during transport is further investigated using the CAABA/MECCA box model. It seems that the reviewer has overlooked the fact that there is a very small strip of land between our site and the sea, so emissions of short lived gases such as isoprene must be fresh, i.e. local. b) The steep decrease in relative humidity and the parallel increase in ozone are a strong indication that the site was impacted by the free troposphere. This is

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because ozone is rapidly deposited to surfaces in the boundary layer and the free troposphere is cooler and drier. A further graph showing the diel cycle of ozone is added to support this point. Ozone mixing ratios are on average higher at night. This indicates that the site is in contact with the free troposphere. Otherwise the mixing ratios would decrease strongly during the night due to the high dry deposition rate for ozone and the low height of the nocturnal mixed layer. This shows that the transport from the free troposphere plays an important role.

The above text (and accompanying figure) is now added to explain this point more clearly:

(see reply figs 4 and 5)

14. I am not convinced the usefulness of diel variability analysis for the whole campaign given there are clearly several meteorological/transport conditions during the period, while the paper still spend much effort to discuss the overall diurnal pattern, median vs mean values, etc. How about discuss those main transport conditions in more details?

As suggested by the reviewer we now expand figure 6 to include diel cycles from both the east and westerly flow regimes. The point we are making remains the same. There is no evidence of a consistently different diel cycle in the oxygenated species that could be related to different local emissions from the short strips of land between sea and site to the north and to the west. The measured mixing ratios of the OVOCs are predominantly determined by emissions and subsequent photochemistry remote from the site. For the acetic acid data a clear diel cycle emerges only during one section of the data which is analyzed in greater detail in section 3.2.1. This means that the short strip of land between the site and the sea does not significantly impact the measured mixing ratios of the oxygenated species shown here.

We now add the following text to reinforce this point. “Figure 6 shows the diel cycles of the oxygenated VOC species in the eastern and western European flow regimes. There is no evidence of a consistently different diel cycle that can be related to local

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emission or photochemical production over the short strip of land between sea and site. The measured ratios of these compounds are rather determined by emissions and photochemistry remote from the site."

(see reply fig 6)

15. Ozone seems to be a good indication for fresh/aged air too. And the observed ozone is high. Are they coming from free troposphere, or are they from aged air? These could give insights on the VOC analysis particularly for acetic acid, but are lacking in the current version.

We take the reviewers point and refer them to our answer to 13b above. A further graph of the diel cycle of ozone and accompanying text has been added to support this point.

16. Section 3.2.2: It is not clear how useful the box model is. Are the conclusions already well known? Given the boxing model is not constrained at the local scale, it seems to be not necessary to this paper.

In this paper we attempt to determine the main processes causing variation in our measured species, particularly the OVOC species. In this context the box model provides valuable information as it can provide chemical mechanism based estimates of the rates of production and loss of our species during transport. For example we use the model to show that the acetic acid photochemically produced during transport is inadequate to explain the measured mixing ratios and that an in-mixing from the free troposphere must be invoked to realistically explain the measured data.

17. Page 14, Line 447-451: a) Photolysis rate cannot be neglected for acetone given it is 1/3 -1/2 of its loss terms. B) How is OH measured? It is not mentioned in the method.

a) The photolysis loss rate is small in comparison to the loss through OH, particularly in the boundary layer, and can be neglected in this assessment. The OH lifetime (assuming 2x10ˆ6 molecules cm-3 OH) is circa 32days whereas the photolysis lifetime in the

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region, even in the upper troposphere where the photon flux is highest is between 75 and 250 days. Early budget estimations of acetone assumed a quantum yield of one, however, work by Blitz et al 2004 and Arnold et al. 2005 have shown this to be wrong as the yield is temperature dependent. This considerably lengthens the photolysis lifetime. In order to clarify this assumption we insert the sentence, “since the ground level photolysis rate of acetone is at least ten times lower than the loss rate due to OH it is neglected in this calculation.

b) A full description of the OH instrument is now given in the method section. The inserted text is: “Atmospheric OH was measured during Cyphex using the HORUS (HydrOxyl Radical measurement Unit based on fluorescence Spectroscopy) instrument based on the LIF-FAGE (Laser Induced Fluorescence-Fluorescence Assay by Gas Expansion) technique for atmospheric OH measurements. The laser system consists of a tunable dye laser which is pumped by a diode-pumped Nd:YAG laser pulsing at 3 kHz. The sample air (ambient air) in HORUS is drawn through a critical orifice (pinhole size of 0.9 mm) into a low pressure detection cell ($\sim$4 mbar for Cyphex) at 10 lpm, where the OH molecules are selectively excited by 308 nm laser light pulsing at 3 kHz. An etalon, controlled by a stepper motor, causes the laser radiation to be tuned on and off resonance with the OH transition every 7 s, enabling detection of the spectroscopic background. Further, the spectra of the measured atmospheric OH is compared with the one obtained from a reference cell (where OH is produced by H2O photolysis) in order ensure no interferences from fluorescence of species like SO2 and naphthalene. The chemical background (equivalent to the OH produced in-situ during the travel from the pinhole to the center of the detection cell) is accounted for by the IPI (Inlet pre-injector), mounted on top of the nozzle (Novelli et al., 2014). The IPI is used to inject an OH scavenger (3-5 sccm of pure propane at a flow of diluted with 8000 sccm synthetic air for Cyphex) at the inlet, periodically every 2 minutes, resulting in alternating measurements of background OH (with scavenger injection) and total OH (without scavenger). The difference between these two signals gives a measure of the atmospheric OH at a time resolution of 4 minutes. Calibration is achieved by measur-

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ing the signals generated by known amounts of OH (Martinez et al., 2010), which are produced by irradiating pre-measured humidified air with 185 nm radiation (generated with a calibrated lamp). The precision for OH measurements is 4.8e5 molecules per cc for 4 min time resolution. The accuracy for OH measurements is 28.5% (2σ)."

18. Page 14, line 459: a few place mentioned PBL height 500m. Is this a good assumption for this region?

We believe that 500m is a good assumption for the marine boundary layer height in this study for the following reasons. Taking the definition of the boundary layer from Stull et al. (An introduction to Boundary Layer Meteorology) we take the boundary layer as being "the part of the troposphere that is directly influenced by the Earth's (or Sea) surface, and responds to surface forcings on a timescale of an hour or less. Ceilometer data from the site (height 650m) revealed an average of 250 m for the PBL (total height 900m). The boundary layer over the sea relevant to this study will have been lower than this due to the orographic and thermal effects of the land. Previous aircraft studies in the region (Holzinger et al. 2005) focused on acetonitrile have reported vertical profiles over the sea that show sharp decreases in mixing ratios from 500m to 250m also supporting the 500m boundary layer over sea assumption made here.

Previous regional studies have divided the atmosphere differently in the vertical dependent on the focus of the study. For example Lelieveld et al. 2002 considered the lower atmosphere including 0-4km and Traub et al. 2003 et al. 0-2km (due to model resolution), although generally over continents values of 1-2 km are considered for the boundary layer height in high pressure regions (Stull 1988). Marine boundary layer heights are generally lower and more stable because of the high heat capacity of water and correspondingly lower forcing changes. In the revised version we will support this boundary layer height assumption with the above text and point out that dry deposition rate will scale with this number.

Furthermore we will compare to terrestrial measured deposition rates. For example

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"Hartmann et al. (1991) determined a dry deposition rate of 0.5–1 cm/s for acetic acid in a savanna region. A boundary layer height of 250m (as measured over the site) and an average acetic acid mixing ratio of 1 ppbv during the day would result in a loss rate of 0.07–0.14 ppbv/h. The measured loss rate in Cyprus (0.08 ppbv/h $\pm$ 0.04 ppbv/h) is quite close to these values, which suggests that dry deposition is the major loss process of acetic acid.

19. Page 15, Line 484: again, the role of free troposphere should be clarified, and ozone could be helpful.

See reply to point number 13.

20. Page 15 Line 495: Ocean's role for OVOCs: Could correlations with DMS be more helpful?

The reviewer is suggesting using DMS as a marker for ocean influence that can be used to elucidate the OVOC behaviour. Unfortunately, the process that produces marine DMS is different from the marine production and loss processes of the other OVOCs making this approach uncertain and complex. DMS is produced by certain marine microorganisms via enzymatic cleavage of DMSP, and as it is insoluble in water it is rapidly emitted to the air. Thus in productive regions there will be emissions and oligotrophic regions (like parts of the Eastern Mediterranean) not, and the location of these regions varies with time. The much more soluble acetone has been observed to be emitted by day and uptaken by night from seawater in productive waters, and when productivity decreases it can be uptaken all day. This is due to microbial consumption in the surface layer that creates a concentration gradient between air and water. Methanol is similarly consumed by microorganisms, however, a significant photochemical production mechanism exists in the aqueous phase, particularly in productive waters. (Millet et al. 2008, Sinha et al. 2007, Dixon et al. 2014). Thus the correlation with DMS was not used.

21. Section 3.2.4: I don't get too much information from this section. What is the main

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point? The lower CO emission for this region is interesting, but so do anthropogenic VOCs. An analysis based on transport pattern or aging would be more interesting. The purpose of this section is to provide correlation coefficients for the main species and variables studied here, for comparison with previous measurements (to observe regional emission changes e.g. lower CO emissions regional relative to 2003), for comparison with data from other regions by other practitioners, and for comparison with future studies in this region. Currently discussions are proceeding to create a large permanent measurement site on the west of Cyprus, so this CYPHEX dataset can provide an important first set of ratios with which future measurements can be compared. In the revised manuscript this section will however be made more concise.

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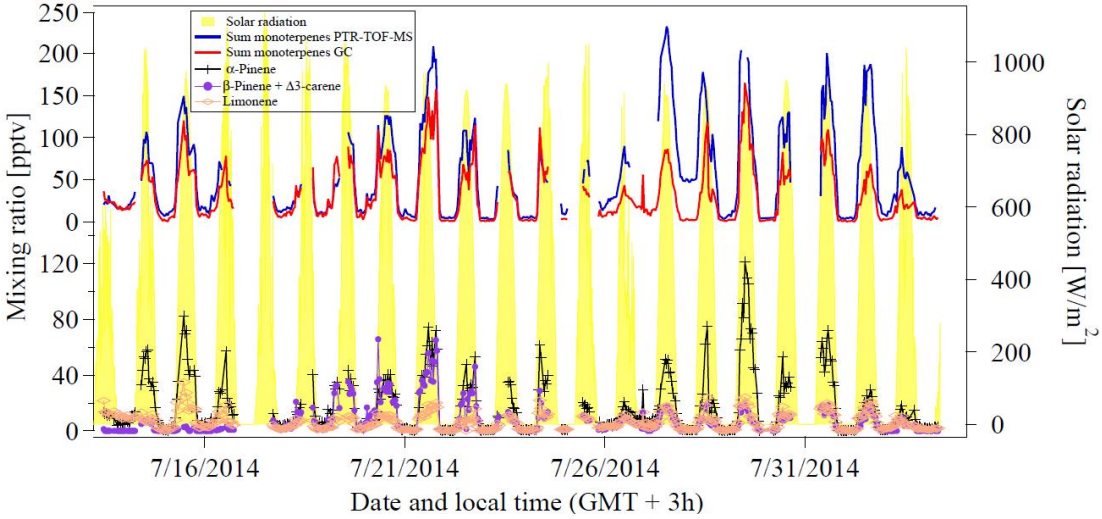

Fig. 1. reply fig 1

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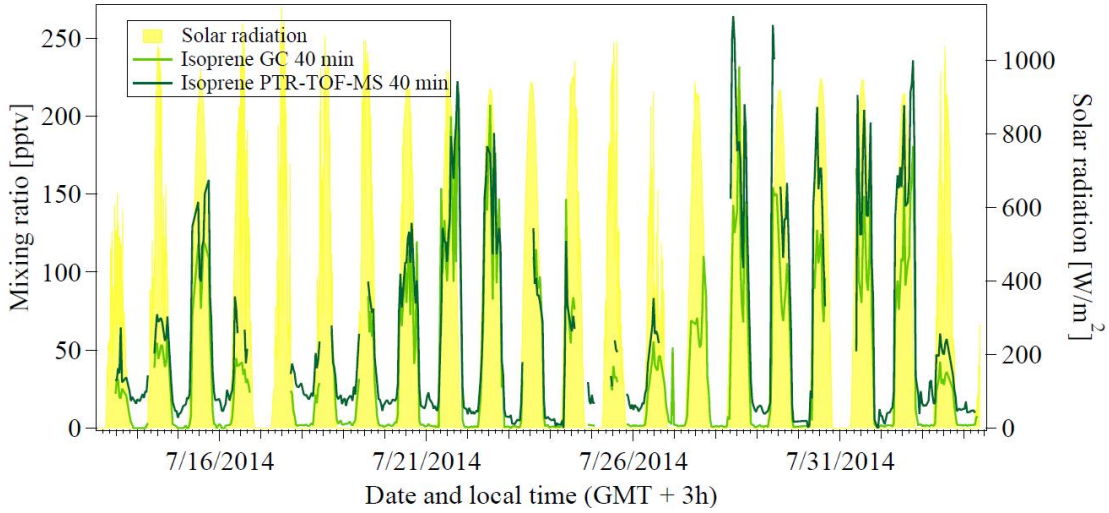

Fig. 2. reply fig 2

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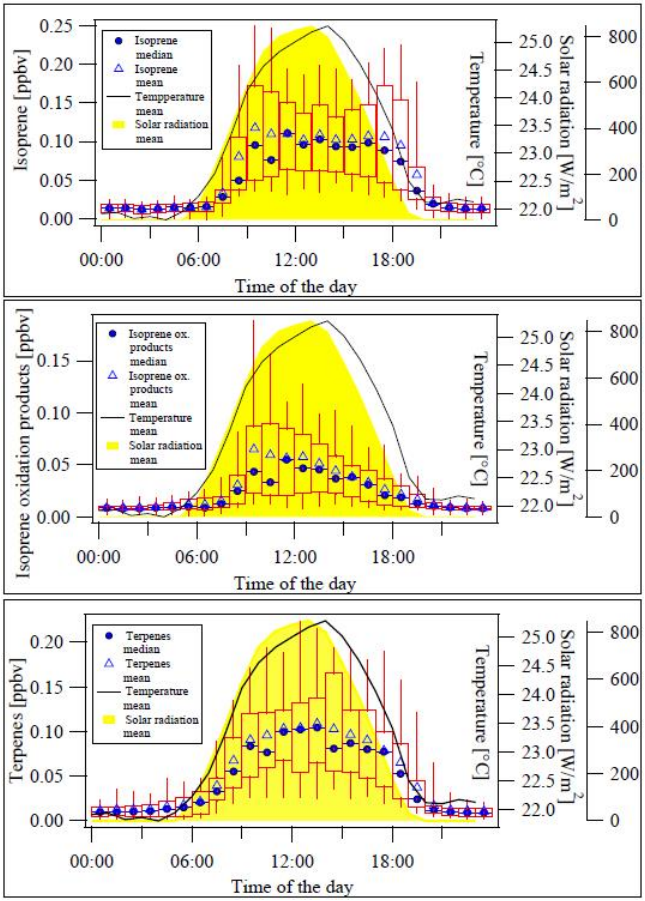

Fig. 3. reply fig 3

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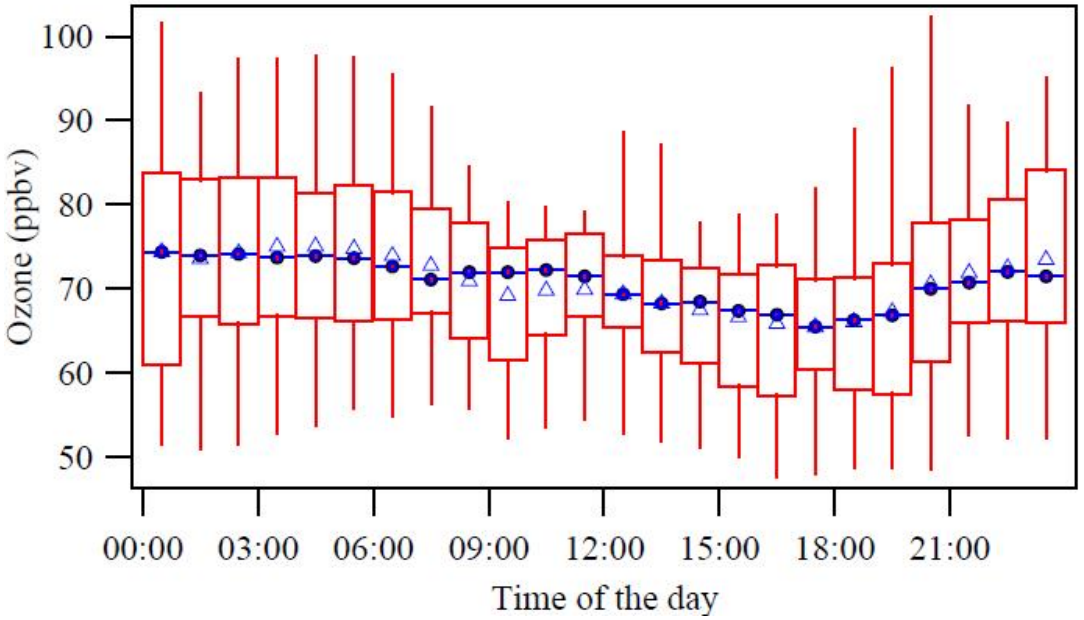

Fig. 4. reply fig 4

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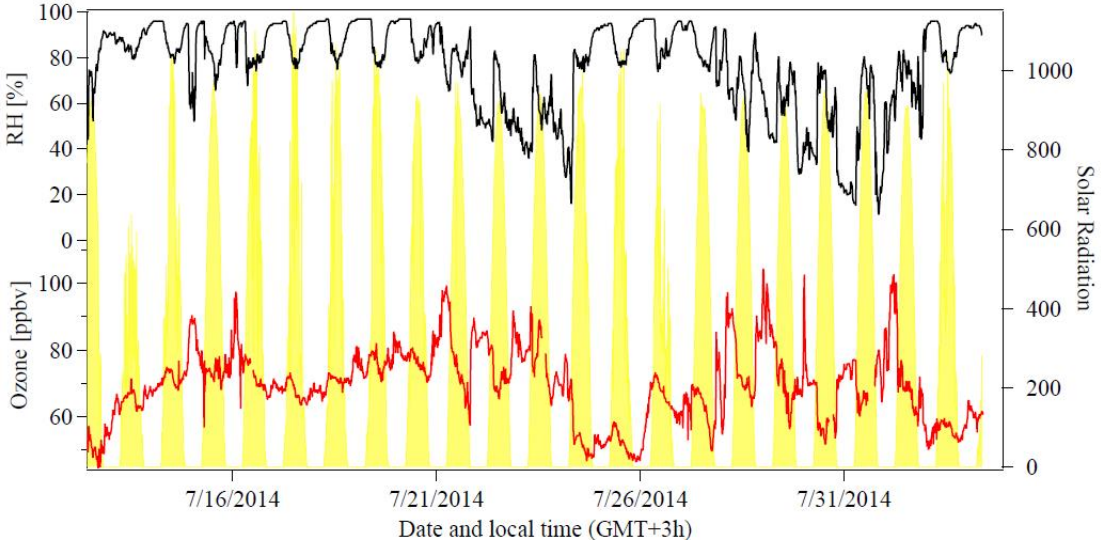

Fig. 5. reply fig 5

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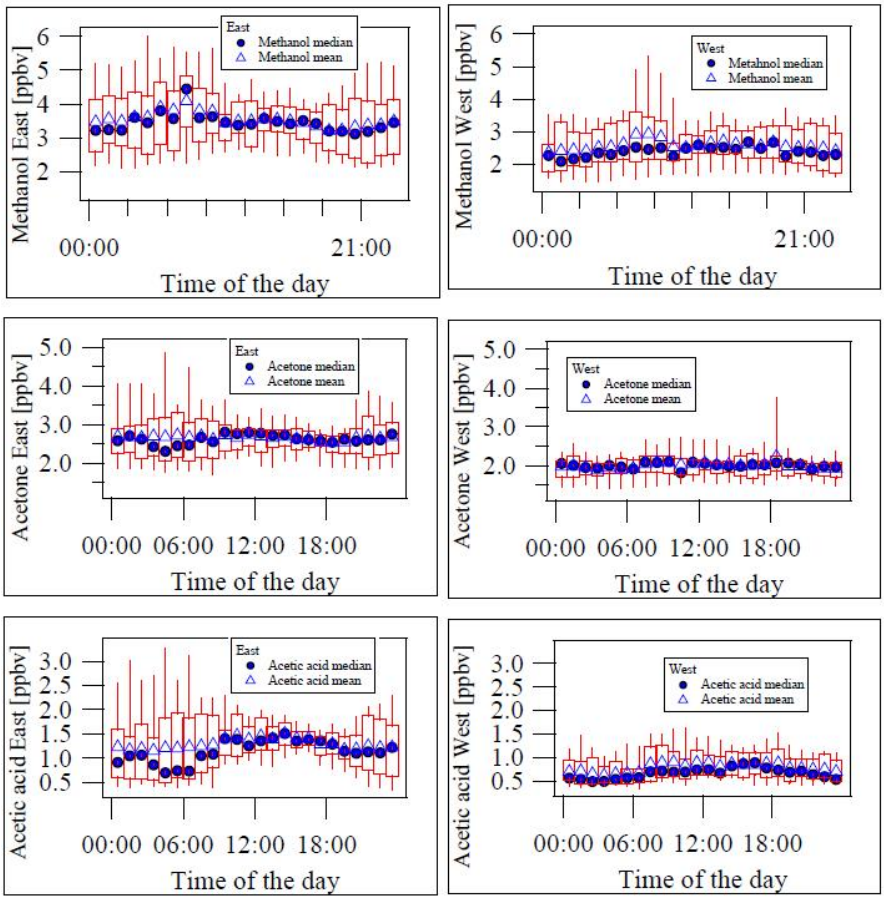

Fig. 6. reply fig 6

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