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Atmospheric Measurement Techniques Discussions

Interactive comment on "A five year record of high-frequency in situ measurements of non-methane hydrocarbons at Mace Head, Ireland" *by* A. Grant et al.

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The authors would like to thank reviewers for their constructive and useful comments. Below we have answered the two reviews separately and answered individual comments separately.

Reply to Reviewer #1

Comment 1: The paper is rather limited in terms of interpretation. . ..

Reply: We apologise for this misunderstanding. The aim of this paper was to detail the instrumental measurements of the NMHCs and to present the long-term dataset of

NMHC measurements at Mace Head. A full interpretation of these long-term data is to follow in a further publication. To clarify the context of the paper we have added a few lines putting the work in context, see lines 54-56

Comment 2: There is a mismatch in the data interpretation that is described in the text and the level of detail provided in the manuscript. For example the NAME modelling classifies air masses into a number of different source region types, but the Tables give only baseline and European values.

Reply: This is because these two air masses form the majority (>70%) of air transported to Mace Head. This has now been highlighted in lines 175/178.

Comment 2 contd.: Similarly the only figure showing actual data is for the full unfiltered data set including local influences, rather than separate plots for different types of air mass. Most readers will be interested primarily in graphs showing baseline trends in NMHCs, but this key information is only given as a single % figure and not in graphical form.

Reply: The reviewer is correct, so we have now added another figure(3) showing baseline data with monthly baseline averages computed using the NAME model.

Comment 2 contd.: The apparently dramatic five year upward trend in toluene can't be visualised since data isn't shown. Clearly this is a species prone to local contamination and one would want to see the variability of this compared to other species.

Reply: We have decided to remove aromatic species from analysis in this manuscript to enable further work to be carried out on their calibration.

Comment 3: Whilst one might wish this situation to be better, not all synthetic NMHC standards are equivalent, and the primary ppb level standard itself will have uncertainty. For long-term data traceability in publications it seems essential to have exact details on the primary standard used from which other standards cascade. For example is it the same standard cylinder over the full five years, what is the reference number, the

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mother cylinder is prepared from? Also how is the mixing ratio of this standard gas tied to the SI and amount of substance? The question is particularly relevant here since the measurements are not made within the framework of a wider NMHC measurements programme such as WMO-GAW.

Reply: Full details on the calibration has now been included in the manuscript.

Comment 4: There is something of a discrepancy in the definition of baseline in the paper. In line 251 the period of 3 days is used (and also referred to subsequently as the period over which air is likely to be unperturbed with fresh emissions over the Atlantic). This differs from the NAME conditions for baseline that appear to have a more stringent 12 day criteria placed on them. The former conditions would effectively allow ages US air masses to form part of the baseline categorisation, the latter presumably not. Since changes in US emissions will be a major driver of North Atlantic composition, it is important to know whether they are artefacts or trends.

Reply: Apologies for the confusion we may have caused. Yes in fact the baseline air masses have not encountered any significant pollution in the 12 days prior to arrival at Mace Head (as quoted and referenced from Manning et al., (2011)). We estimated that under average wind conditions it may take approximately 3 days for an air mass to cross the Atlantic which is why this value was referred to. The text has been modified to clarify the model classification of baseline.

Comment 5: Why should the concentrations of aromatics for example be $\sim$0 ppt after three days transport. Typical mixing ratio measured in outflow from the US east coast (eg from ICARTT papers) are around 100 ppt for toluene. The e folding lifetime averaged over 24 hours, so one might expect of the order of a few 10 s of ppt after 3 or 4 e-folding lifetimes. Whilst mixing and dilution may accelerate this, it is not necessarily to zero values.

Reply: We appreciate that this statement was rather speculative and not quantitative in nature. We have therefore removed it.

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Comment 6: I am not convinced that Pallas necessarily has a higher average OH field than Mace Head in the summer. There is more to this calculation than simply hours of sunlight. This needs estimating using typical ozone and water vapour levels also.

Reply: This quote about expecting summer values from more northern latitudes being expected to be lower for faster reacting species and relating this to the OH concentrations is a direct quote from the paper referenced by Hakola. See lines 270/274.

Comment 7: Table 3 is only meaningful if the [OH] used to generate the pseudo first order rate constant is given. Indeed the value of this table is questionable since it is not of direct relevance to the paper.

Reply: We have added the [OH] used to calculate the lifetimes in the Table. We added this table to familiarise readers with the lifetimes of NMHCS and feel this is a useful reference point when reading the manuscript.

Comment 8: Line 300. There is inconsistency between the reduction in propane noted here from vehicle emissions reductions and line 231 which attributes propane to natural gas emissions and without trend.

Reply: These two statements are different. Line 220 states that during the period we studied (2005-2009) no reduction was seen. But the statement on line 282 refers to why MH 2005-2009 data is lower than earlier years of propane data.

Reply to comments by Reviewer #2

Comment: General remarks: P914, L19: The increase of 34% for toluene seems to be enormous, as this would be the only European site showing an increase for one of the hydrocarbons. Could this be caused by a local contamination or a change of scales?. The only site, which regularly produces data for the European “background” is Hohenpeissenberg and there NMHC concentrations for all species are more or less continuously declining in the last years.

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Reply: We agree with the reviewer and therefore we have removed all aromatic species data from the manuscript as we would like to investigate their calibration further prior to publication.

Comment: P916, L24 – P917, L22: I think the description of the Medusa system should be considerably shortened as everything is already described in the Miller et al. (2008) paper.

Reply: This section has now been shortened.

Comment: P921, L8ff and Table 2: The more or less stable behaviour of benzene is comparable to the other European measurements, because as mentioned the major part of the detected decrease occurred in the years before 2005. The increase in toluene (and to a lower degree those of ethyl benzene), on the other hand, is absolutely outstanding and not in line with all other measurements in Europe (Helmig et al.). Further data which are publicly available are from Hohenpeissenberg (over the WDCGG) and also there the trend actually shows into the other direction. When looking at figure 2, it seems that 2009 was exceptional for toluene at Mace Head. If analysis would have been done with 2008 I assume that results would possibly have looked different. This could be discussed in order to not over-emphasize this result. This feature would possibly be worth to have a closer look using some additional analyses (e.g. LPDM to detect the source region, or wind speed for local contamination). That this feature seems to be practically independent of the occurrence of pollution events or background conditions makes it also rather suspicious. Apart from the usage as solvent toluene is also emitted from car exhausts. I strongly advise to check this toluene and ethyl benzene data in conjunction with other NMHCs and/or an independent tracer such as CO using for example x-y plots. This should also be done for the different years in order to see if there is a step change or an overlying trend. Also here the Hohenpeissenberg data could serve as a point of reference.

Reply: We have decided to remove aromatic species from analysis in this manuscript

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as we would like to investigate their calibration further prior to their publication.

Specific remarks

P914, L13: Start a new sentence: . . .hydrocarbons. Largest. . .

Corrected line 22

P914, L22: Include the citation

This was included line 358

P915, L4: There are longer times series around for the analysis of trends of tropospheric O3. See for example the review of Oltmans (Atmospheric Environment 40 (2006) 3156–3173, Long-term changes in tropospheric ozone) and the last IPCC report.

A reference has been made to this more recent paper by Oltmans line 37

P915, L16: isoprene is not mentioned anywhere else, so I assume it was measured but will not be reported.

Apologies this has been removed

P916, L16: The measurement system

Corrected line 77

P916, L19: I would propose that you cite Miller et al. (2008) when you mention the Medusa system for the first time.

We agree, see line 79

P916, L25: . . .with analysis of the same. . .?

Corrected line 85

P916, L28: Producer of the cryotoger?

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Included line 88

P918, L6: Is there some information only mentioned in Yates (2007) or is it also contained in Yates et al. (2010)? If so, please also cite Yates et al. (2010), as this is easier to access than the PhD work. (and line 9).

No extra information of relevance to this manuscript is provided in Yates 2007. This has now been replaced by Yates et al. (2010).

P918, L17-20: Some of the ions do look strange or even impossible, please check carefully: e.g. C2H2 65(m/z)?? for ethane and pentanes?

Apologies about these errors they have been corrected line 129

P918, L22: I don't understand these blank corrections for benzene and toluene. How big were they and what is the difference with the values shown in table 1?

The revised manuscript does not report aromatic species

P918, L27-29: This is somehow not the right place to mention these additional measurements by the same instrument. Perhaps it can be omitted or can be mentioned just after the general description of the Medusa.

Okay, this has been moved to line 98

P919, L25:Perhaps also the initial NAME publication from Ryall et al., should be mentioned here, as it is publicly available.

This publication has now also been referenced.

P921, L3: The Mann-Kendall test tests. . .

This has been corrected as suggested

P923, L1 and Table 3:. Please specify the OH number density for the calculation of the lifetimes.

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The [OH] has now been quoted in Table 3.

P923, L16ff . . .at Mace Head in comparison with other European background measurements.

I'm afraid I don't understand this comment

P923, L18. This should not be _0. Let's assume a source of 200 ppt (which is quite moderate). This would take around 6 days until 2.2 ppt are reached. This is enough time for intercontinental transport and within 3 days concentrations would still be around 20 ppt. Thus authors should be more careful with their assumptions about sources in the background air. This does not exclude ships from being important, but then the same explanation should be valuable for all the other NMHCs from fossil fuel exhaust.

This statement was speculative and not quantitative in nature, we have therefore removed it.

Table 4: use NMHC instead of VOC for consistency. The Lewis et al. (1996) should be Lewis et al. (1997) and it should be labelled campaign instead of cruise

No this is correct as this year is quoting the year in which measurements were actually taken. Yes you are correct this should be labelled a campaign. Apologies this was a typesetting error.

P924, L25: the solar zenith angle is however lower, so the average OH radical concentration is possibly not really higher than in Mace Head.

This comment has been modified to quote directly from the paper see lines 255/258

P925, L1ff: Dollard et al. also see the same trend as for propane for nearly all other hydrocarbons. They also mention propane sources from natural gas leakages and industrial emissions. So this should also be included into the analysis.

This has now been included in the discussion. See lines 273/274

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Please also note the supplement to this comment:
http://www.atmos-meas-tech-discuss.net/4/C514/2011/amtd-4-C514-2011-supplement.pdf

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Interactive comment on Atmos. Meas. Tech. Discuss., 4, 913, 2011.