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Atmospheric
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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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Short Comment by Christian Plass-Duelmer and Detlev Helmig

We appreciate this group's effort to utilize the Medusa instrument for the continuous monitoring of volatile organic compounds (VOC). This research will hopefully motivate other Medusa users to include VOC in their monitoring program. Data generated from these measurements will be a valuable addition to the World Meteorological Organization Global Atmospheric Watch VOC program (GAW 2007, Helmig et al., 2009).

This publication presents an interesting set of non-methane hydrocarbon (NMHC) data in the atmosphere from a marine station that is impacted by air from rather diverse

source and emission regions. The manuscript raises some questions concerning results from the Southern German site Hohenpeissenberg (that were included in (Helmig et al., 2009)), which we would like to clarify. The monitoring method and first results of this program were presented by Plass-Duelmer et al. (2002, 2007). Furthermore, newer data and interpretations were recently presented by Schneidemesser et al. (2010). Briefly, this monitoring builds upon daily, noon-time collection of ambient air samples with subsequent in-situ analysis by an on-site gas chromatograph-flame ionization instrument at Hohenpeissenberg. Trends are derived from a harmonic/exponential fit to the monthly averaged data. Please note that these trends are therefore average relative year-to-year changes, rather than the steady linear regression derived trends calculated in this publication.

We would also like to comment on some other points presented in this paper and hope that the authors will find these remarks helpful in their data interpretation:

1. Despite the fact that this monitoring produced an impressive, high time resolution record of five years of data, a five year record is a rather short time period for estimating atmospheric trends. For compounds with atmospheric lifetimes on the scale of these NMHC, atmospheric short term and year-to-year variability due to emission source changes, transport and oxidation chemistry is substantial. A trend analyses should consider those fluctuations. For these NMHC, we recommend a minimum of 10 years for trend determination. As there are several earlier data sets with NMHC measurements from Mace Head available (referenced in Yates et al., 2010), it would be valuable to include those results into this study, to investigate longer term trends and carefully compare those findings with these more recent results and check for consistency.

2. Linear regression through the available data set is a rather crude trend analysis that can be susceptible to errors from occasional spikes or minima in the data, depending on their occurrences in the data set. Given the strong seasonal cycle of these NMHC, a linear regression is also very sensitive to the selected start and end point of the

record (time of year). Unfortunately, those details were not provided in the article for evaluation. We recommend applying a harmonic fit to the data, with possible fourier transform filtering of short frequency fluctuations (for example Thoning et al., 1989; Plass-Duelmer et al., 2007).

3. The discussion about reactive hydrocarbons including propane being above the detection limit in summer is hard to follow. Plotting of the NMHC results on a logarithmic scale may help better illustrating these results. We also recommend abstaining from using the term ‘zero concentration’, as analytically this terminology is incorrect. It would be better to label those measurements as less/equal the instrument detection limit.

4. Figure 2 includes a number of data points that are substantially below the background levels typically observed during that time of year. As it appears that these data were not excluded from the analysis it seems that these measurements were considered as reliable results. The authors are encouraged to further discuss the reasons for these deviations.

5. Results of other recent NMHC monitoring programs might be of interest for comparison with the Mace Head results. This includes, i.e., the studies by Gautrois et al. (2003), Helmig et al. (2008), von Schneidemesser et al. (2010), and the yearly EMEP/CCC VOC reports by Solberg covering recent data from European EMEP stations.

6. Stable, or more so increasing levels of benzene and toluene are in contrast to observations from continental sites in Europe (e.g. Solberg, 2010). Most other data have depicted downward trends for these compounds. For Hohenpeissenberg, trends of benzene, toluene, ethylbenzene and p,m-xylene are – (6-7)% yr-1, and these results generally follow trends from European urban areas (von Schneidemesser et al., 2010). The reported increases from Mace Head are therefore rather surprising. We recommend that the authors carefully investigate potential measurement and calibration artefacts. The authors mention that blank corrections were performed for benzene

and toluene, however, the article does not provide details what type of sample was introduced for the blank determination (p. 918), and about the origin and consistency of blanks. Very few other trace level NMHC analytical systems use Nafion dryers. Please indicate if standard experiments at variable moisture levels were performed to test transmission and artefact formation under varying atmospheric humidity levels. As this article is a publication in an analytical journal, we encourage the authors to provide more detail concerning such technical questions.

7. It appears that the calibration scale is based on a single, many years old hydrocarbon standard mixture that was diluted down to ppt levels. It should be clarified if this is indeed the case, and how the authors ensured consistency of the calibration scale over the time of this study. Especially, potential losses of adsorptive compounds like aromatics in the cylinders at ppt levels should be considered. Furthermore, it is unconventional that the authors name an uncertified dilution of a commercially purchased calibration gas of unspecified age into an unspecified cylinder a “primary standard”. Potentially, a loss of aromatic compounds in the “primary standard” might explain the reported results of increasing concentrations of these compounds in the ambient samples. Please also note that there has been an international intercalibration and intercomparison effort for the global VOC monitoring program under the auspices of the WMO GAW. This activity provides a traceable reference gas scale for atmospheric VOC background monitoring. We recommend participation in this effort for further quality control of these measurements.

8. It may also be worthwhile evaluating these in-situ data with the NMHC measurements in the weekly collected samples by the NOAA Cooperate Air Sampling Network at Mace Head. These NMHC analyses are referenced to the WMO-GAW WCC scale. Figure 1 depicts as an example the ethane time series results from this program (data are available at ftp://ftp.cmdl.noaa.gov/ccg/). Please note that these illustrated data were not filtered for air mass origin. Instead, an outlier rejection and smoothing filter routine (Thoning et al., 1989) was applied. Samples retained for determination of the

harmonic seasonal cycle fitting curve are labelled in blue, rejected values in red. The ‘function’ curve shows the harmonic component of the data, the ‘trend’ curve shows the year to year deviations in the data from this curve. The median ethane mole fraction of this data set is 1268 pmol mol-1, and the seasonal minimum and maximum of the harmonic fit function are 487 and 1994 pmol mol-1, respectively, resulting in a seasonal amplitude of 1510 pmol mol-1.

9. In section 3.3 the authors speculate about shipping emissions as the reason for increased summer-time concentrations of reactive aromatic compounds. As mentioned above, a log presentation of the data would help better illustrating this observation. Shipping emissions should likely show up as perturbations superimposed on the seasonal concentration cycle, and it would be expected that this effect should be noticeable throughout the year in samples collected from the “background” sector.

10. It is not clear what summer minima and winter maxima means (p. 923, Table 4). Is it the average in the winter/summer months or is it the monthly maximum or minimum or are these the extreme values of the data? It is also not clear, how results below the detection limit were treated for this determination?

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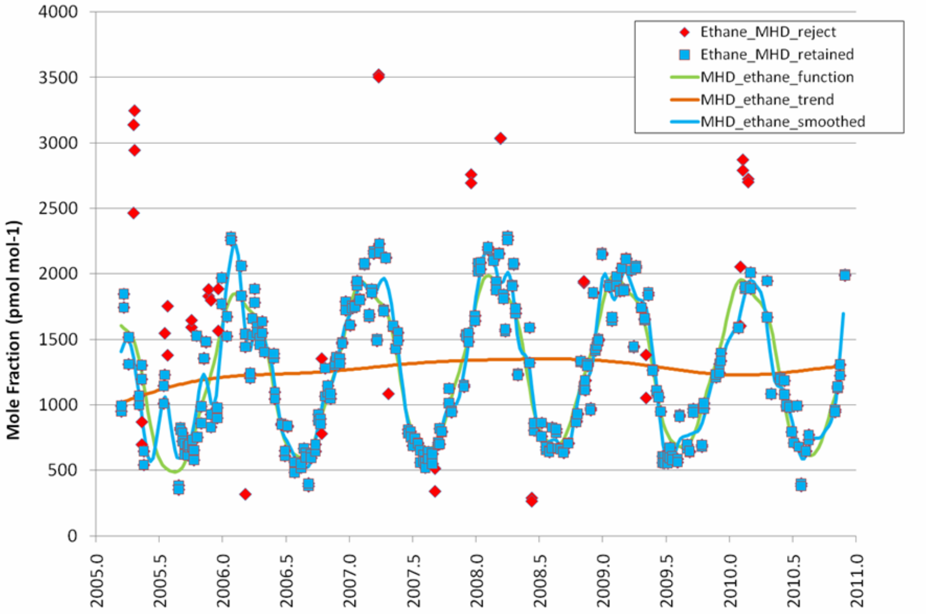

Fig. 1. Ethane in flask samples collected at Mace Head within the NOAA Global Monitoring Division Cooperate Air Sampling Network during 2005-2010 (details see text).