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# NMHCs at the WMO-GAW Mt. Cimone station *trends, seasonal variation and source characterisation*

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# Introduction

- The role of NMHCs in the production of tropospheric ozone is well known;
- It is difficult to derive trends and seasonal cycles from urban sites because of the vicinity of pollution sources.
- Since 2010, continuous high-frequency in situ measurements of a range of NMHCs have been made at Mt. Cimone WMO-GAW Global Station, on the highest peak of the Italian Northern Apennines (2160 asl), at the border between the Po Valley (and the Alps) and the Mediterranean Basin;
- Mt. Cimone is the only remote station South to the Po Valley where NMHCs are measured continuously.



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( 2 )

# Method

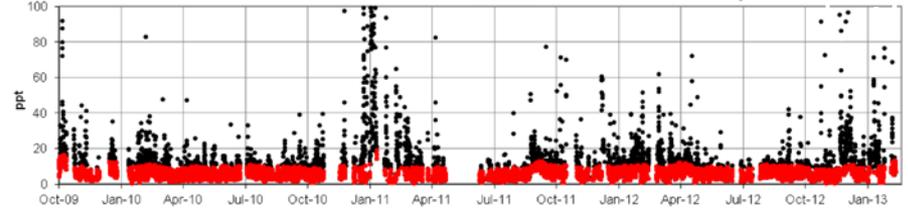
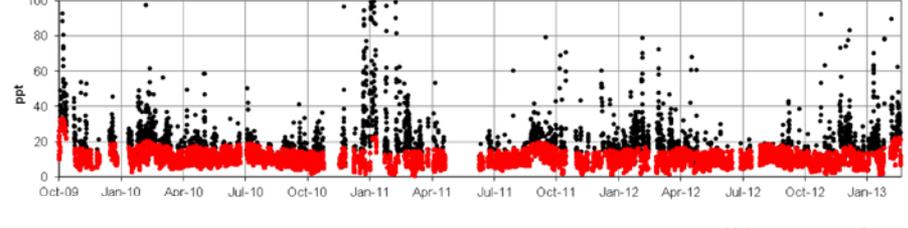
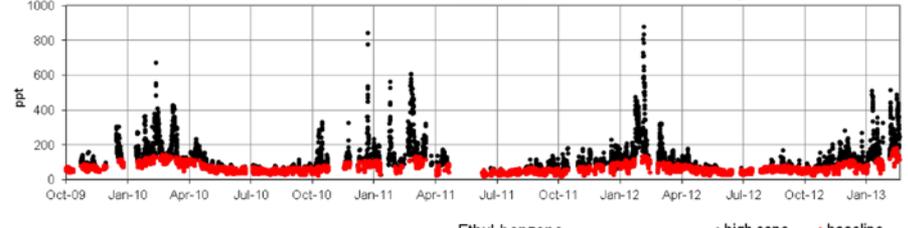
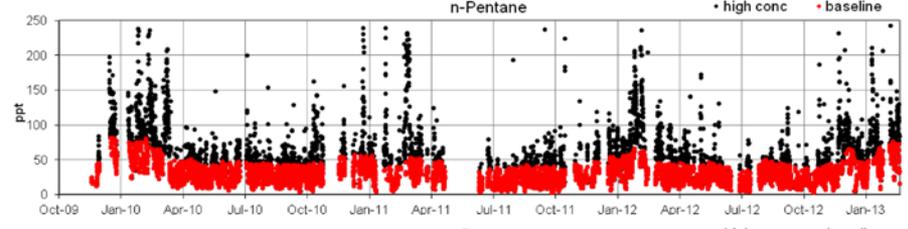
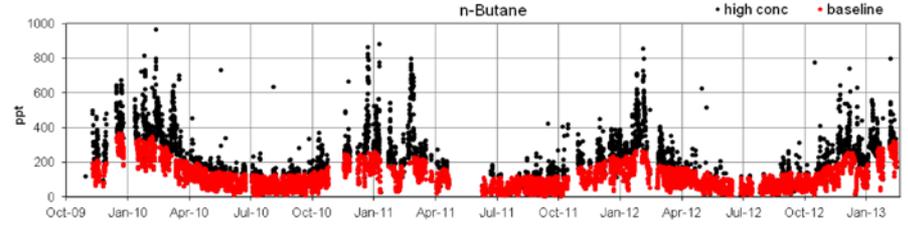
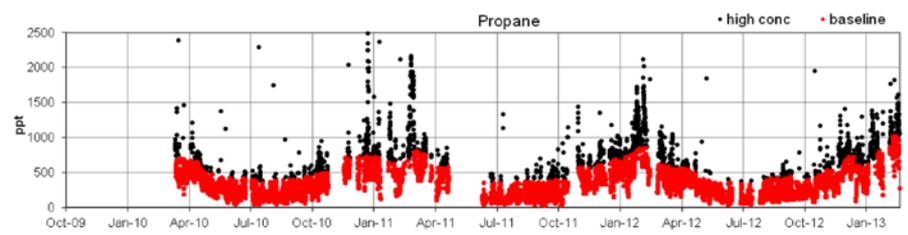
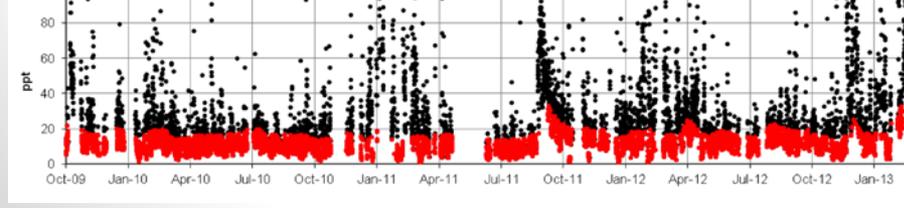
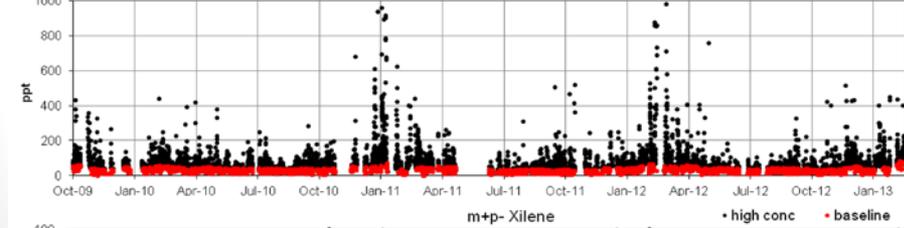
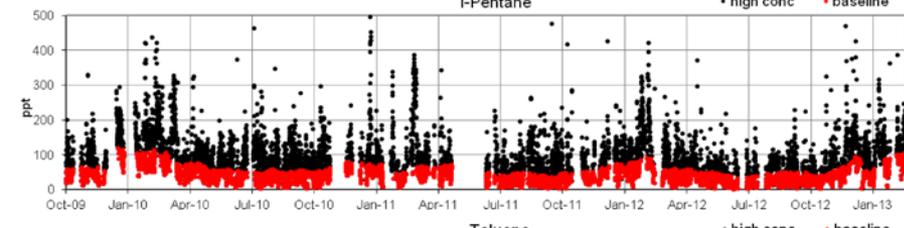
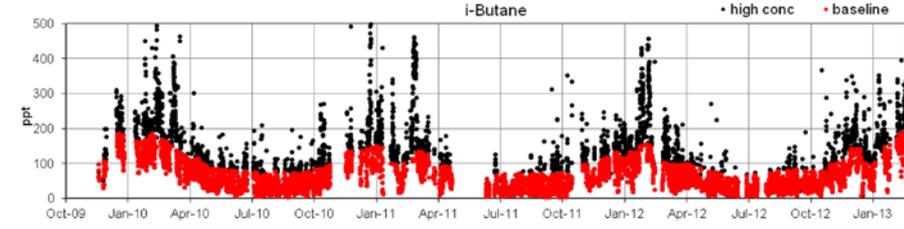
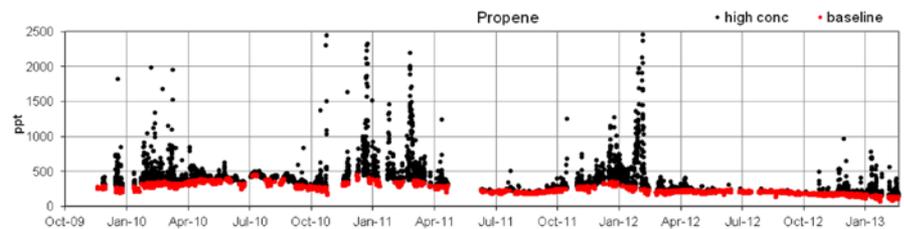
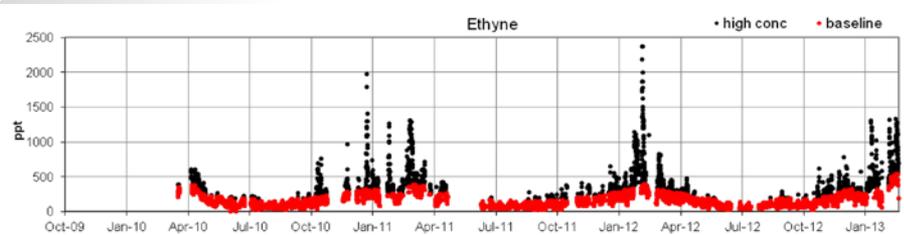
- 1 litre of real air is trapped, every 2 hours, on a multilayer adsorbent trap cooled at  $-30^{\circ}\text{C}$ , then desorbed, separated on a GasPro column and detected by MS in SIM mode;
- Calibration: NPL primary reference gas mixture containing 30 HCs with certified concentration around 4 ppb; absolute concentrations are propagated to a lower concentration standard in air, that is used to calibrate the actual working std with concentration closer to the real air;
- There are still some concerns on the propagation of the absolute mixing ratios for some components;
- Repeatability of measurements for the compounds considered in this study is better than 10%.

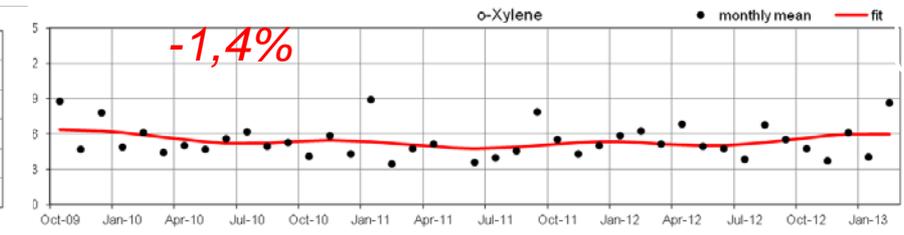
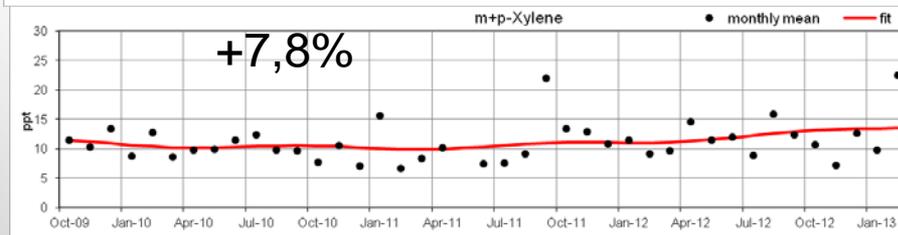
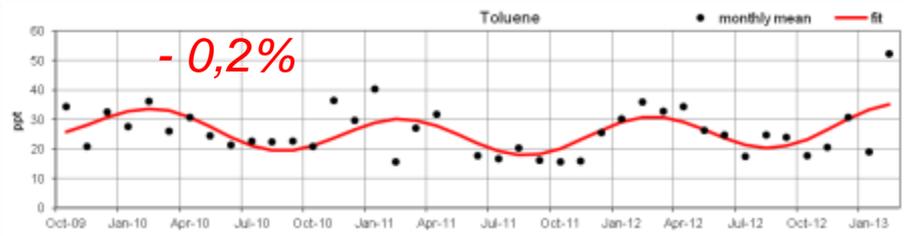
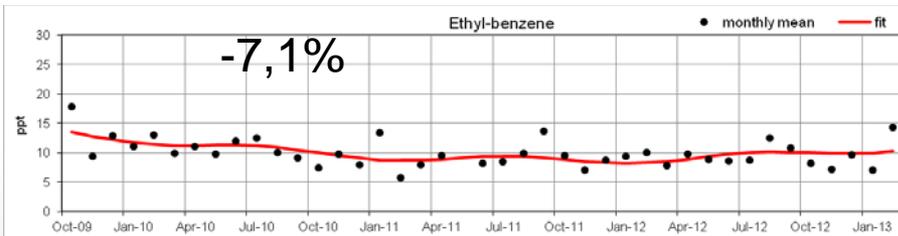
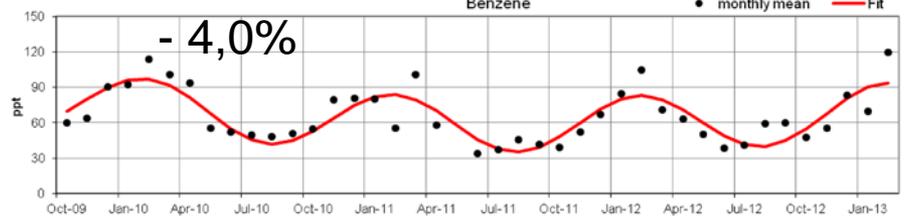
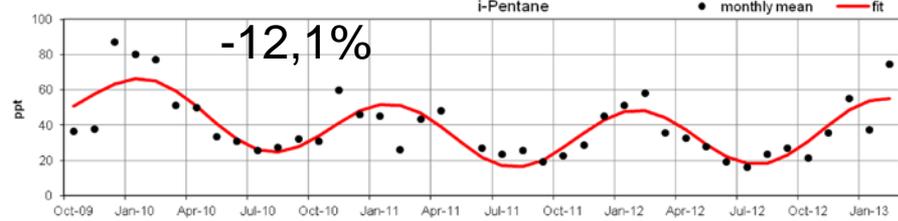
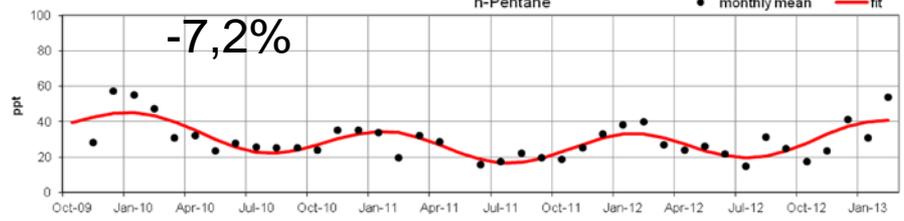
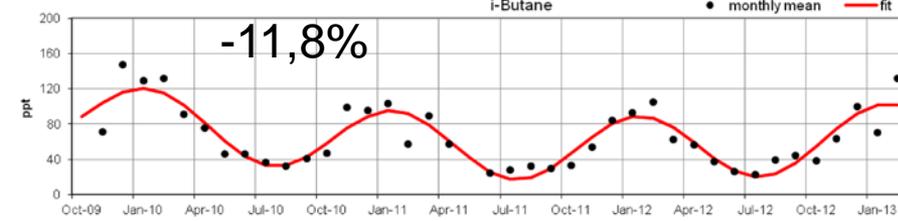
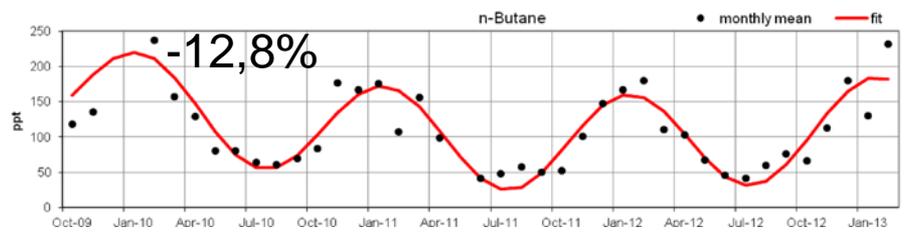
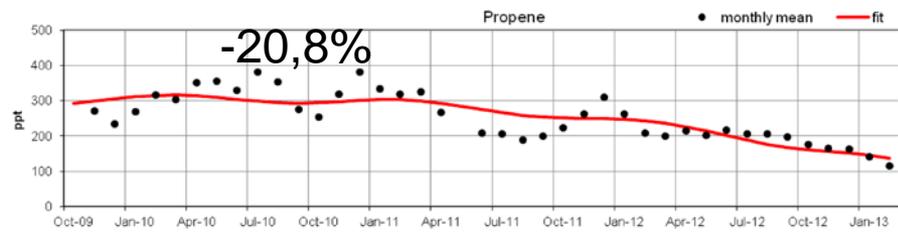
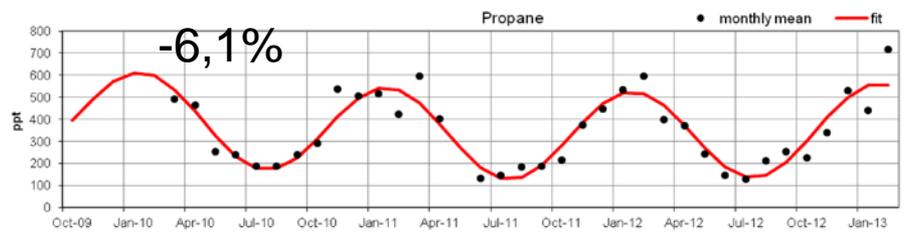
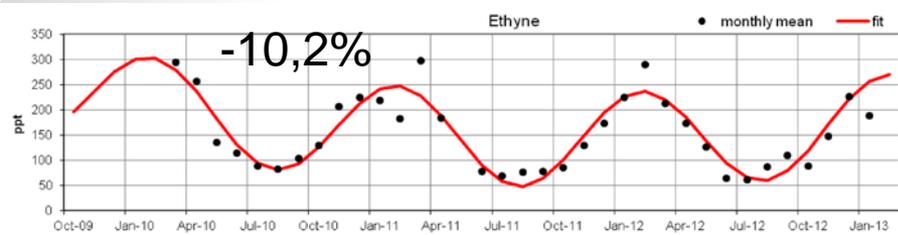


# Method

- The obtained time series are analysed in order to derive concentrations ascribable to “baseline” conditions;
- The background is evaluated through a two step statistical methods (Giostra et al, 2011) based on the assumption that “baseline condition” data and “not baseline” data follow two different statistical distribution that are analytically distinguishable;
- Trends are calculated using a polynomial function fitting the monthly average baseline values.

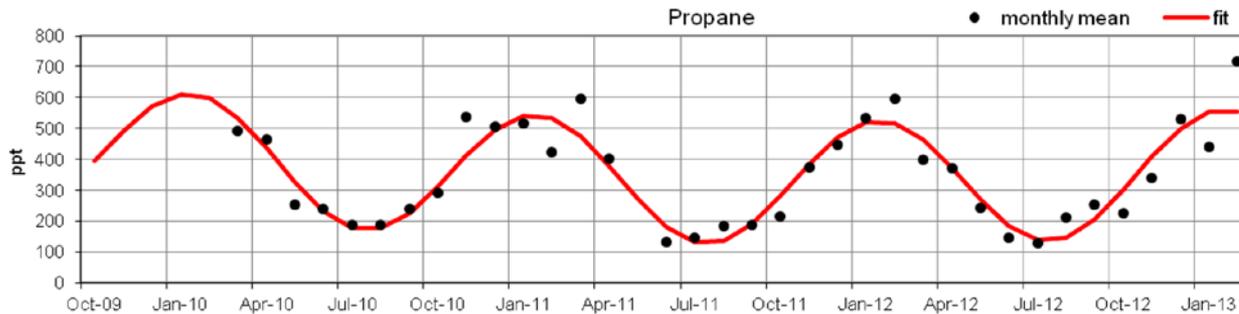






# The propane photochemical clock

(Rundolph and Johenen, 1990)



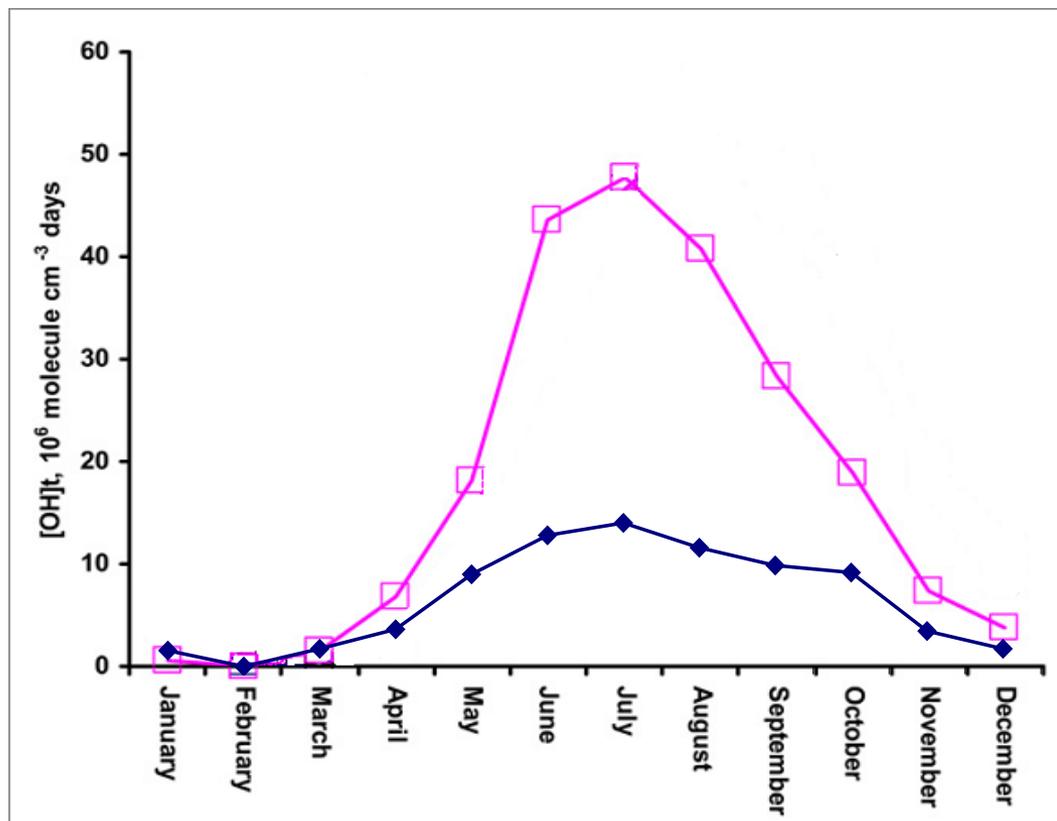
Propane is a purely anthropogenic NMHC with a lifetime of ca 11 d, whose winter maxima are relatively unaffected by the reactivity with OH, thus reflecting its relative emissions. From its monthly depletion relative to the wintertime maximum the monthly time-integrated OH radical concentrations  $[\text{OH}]t$  can be derived:

$$\ln[A_0/A] = K_{\text{OH}}[\text{OH}]t$$

$A_0$  = Propane winter maxima

A = Propane mixing ratio

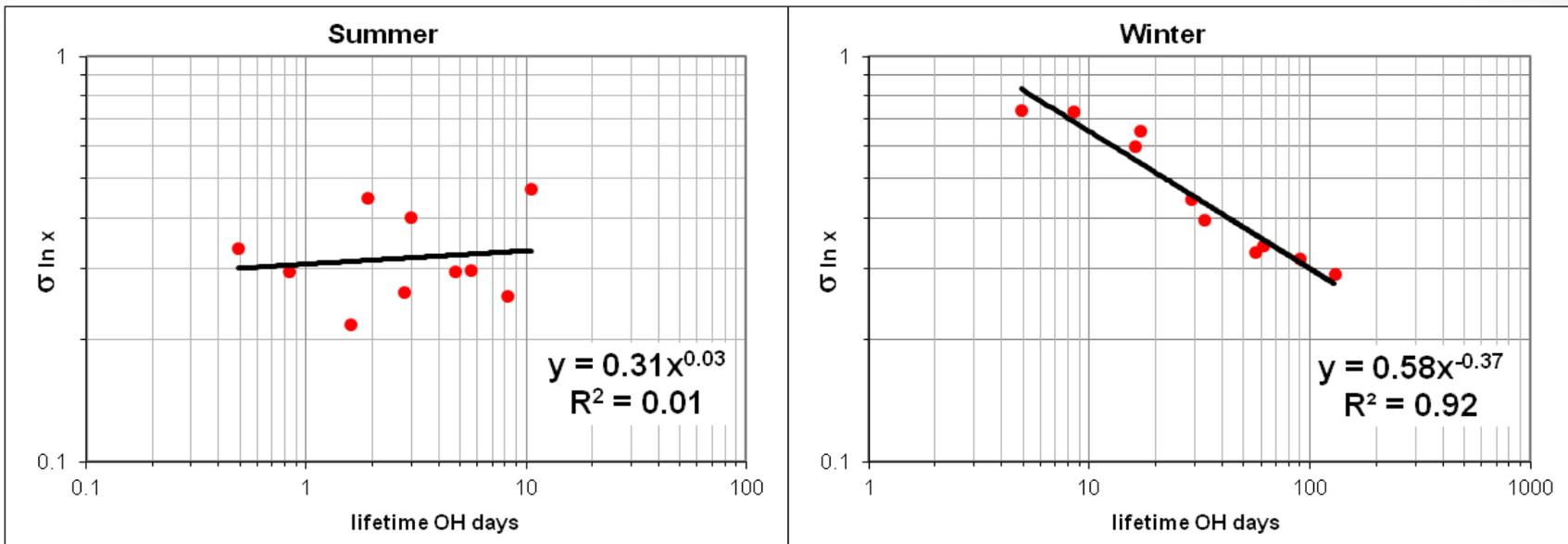
# Seasonal cycles of the time-integrated OH radical concentrations $[\text{OH}]_t$ obtained with the propane 'clock equations', based on propane observed average baseline mixing ratios 2010-2012.



- Mace Head, Derwent et al., 2012 (reference period 2005-2009)
- ◆— Mt. Cimone, this study

Are we underestimating summer values because of the different conditions observed at Mt Cimone during the summer?

# STD of ln of NMHC mixing ratios (all data) against their estimated OH lifetime



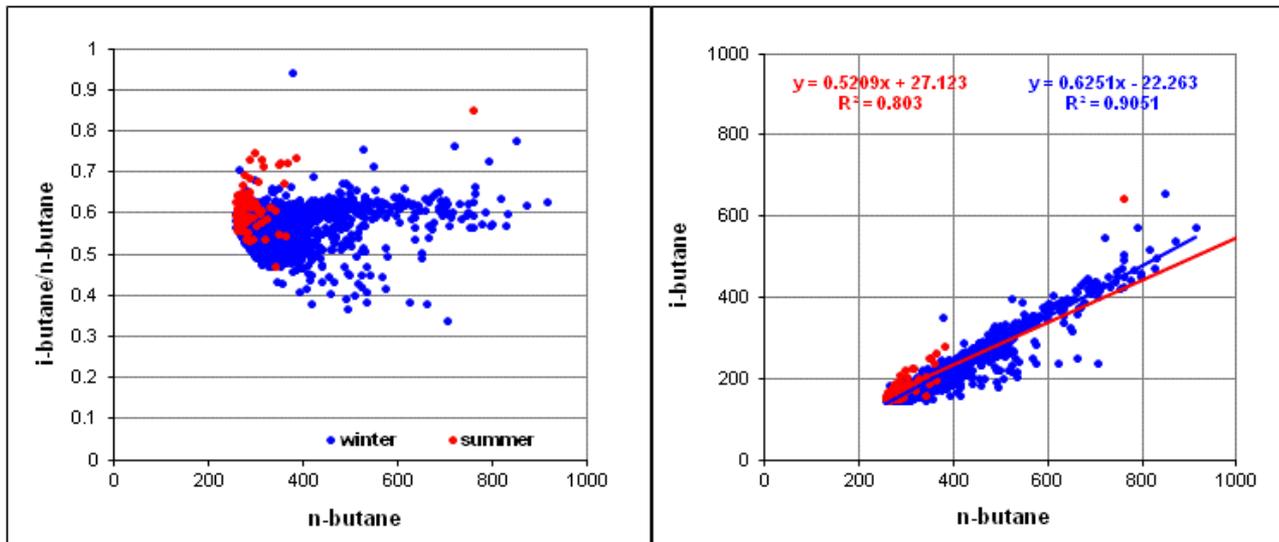
- b gives an indication of the influence of the mixing on the variability, with higher value in case of strong photochemical loss processes and low influence of the mixing and emissions (typical of the winter season) and lower values for dominating mixing and fresh emissions. (Jobson et al., 1998)
- For the free troposphere this value is typically 0.28-0.56 and for urban areas is close to 0;
- At MtC
  - Winter value (DJF) → **0.37**
  - Summer value (JJA) → **0.03**

# Ratios of NMHC isomeric pairs: Seasonal analysis of alkanes isomers during 2010-2012

- Main sources are linked to the use of fossil fuels:
  - Combustion
  - Evaporation
  - Production and refinery
- The ratio of alkanes pairs (enhancements above the baseline) can be used to observe the effects of atmospheric transport;
- Given the similarity in atmospheric lifetimes of the alkane isomer pairs, the ratio at the emission source is preserved at the receptor.

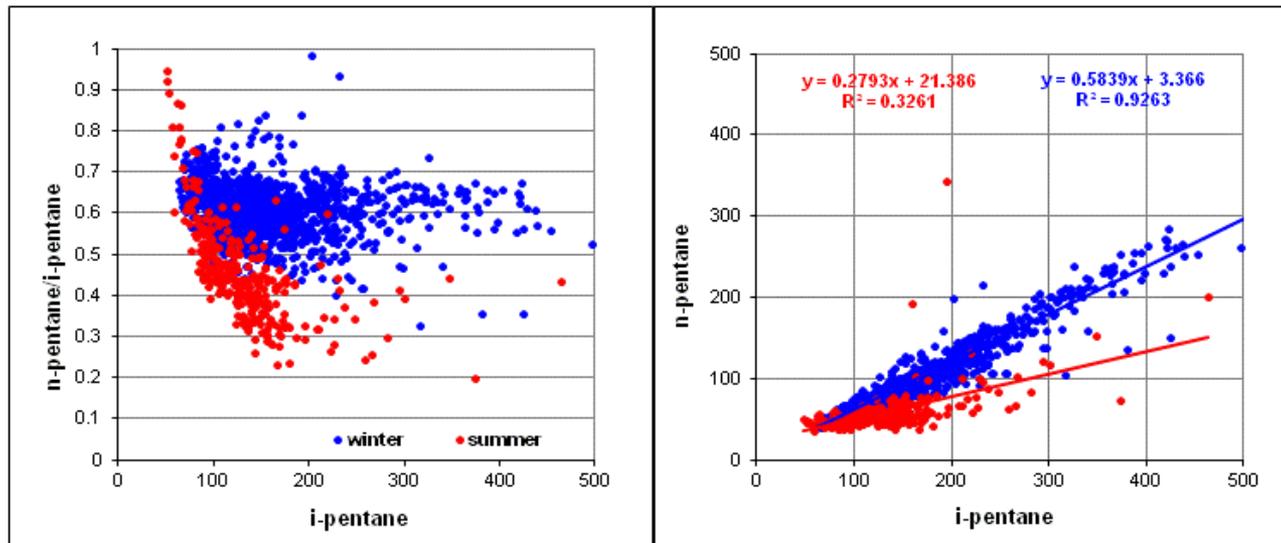


# i-butane/n-butane versus n-butane (left) and i-butane versus n-butane (JJA - DJF)



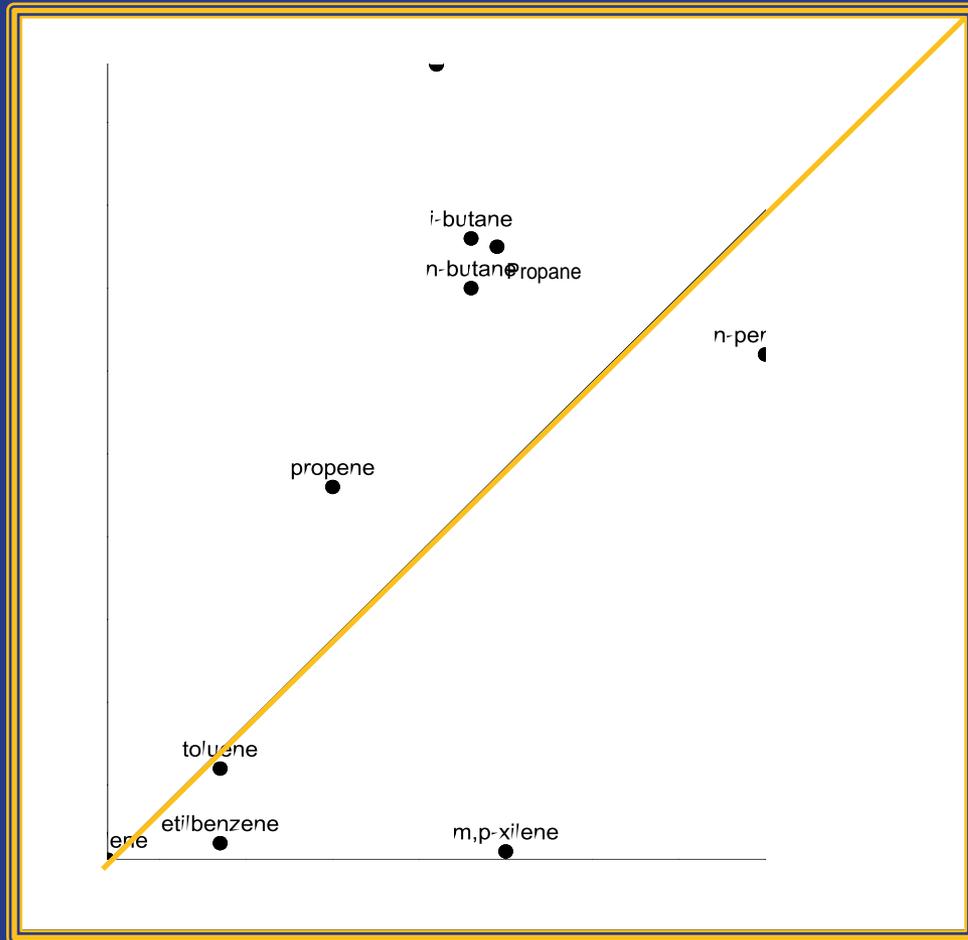
- Ratios at MtC are higher than the 0.45 reported by Yates et al. (2010) at the Mace Head remote site which is the same as at urban sites (Derwent et al., 2000), suggesting that MH is receiving polluted air masses mainly from the same sector;
- At MtC is likely that a mixing of air masses with different origin occurs;
- The summer ratio is slightly higher than the winter one (0.66 vs 0.60).

# n-pentane/i-pentane versus i-pentane (left) and n-pentane versus i-pentane (right) (JJA - DJF)



- The winter and summer correlations are markedly different, suggesting a seasonal variation of emissions;
- The winter value is similar to that reported by Yates et al., 2010 and Helmig et al., 2008 for the free troposphere, meanwhile the summer value is lower;
- Further investigation is needed taking into account back trajectories analysis.

# Identification of NMHCs sources at MtC by correlation with ethyne and i-pentane



Ethyne is a typical product of fossil fuel combustion and a major indicator of vehicle exhaust; i-pentane is a marker of evaporation of fossil fuel (Barletta 2005);

The correlation of ethyne and i-pentane with the NMHCs measured at Mt. Cimone has been calculated;

Those compounds better correlated with ethyne are likely to be linked with vehicular traffic. ( 13 )

# Conclusions

- NMHCs measured from 2010 to 2012 at Mt. Cimone show a decreasing trend which is in agreement with other studies conducted in Europe;
- During the winter months, Mt. Cimone is behaving as a remote site. However during the summer, Mt Cimone differs from other remote sites, being more affected by local sources;
  - Winter time data → long term variability, trends
  - Summer time data → short term variability, emissions
- Emissions of the NMHCs measured at Mt. Cimone are associated mainly to traffic emissions;
- Further investigations are needed, including back trajectories analysis, to better constrain emission sources.



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