

## ***Interactive comment on “Tropospheric OH and Cl levels deduced from non-methane hydrocarbon measurements in a marine site” by C. Arsene et al.***

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Interactive comment on “Tropospheric OH and Cl levels in a marine site” by Arsene et al. Arsene et.al.

We would like to thank referee #2 for his helpful comments to improve the manuscript. Changes/additions are performed in the revised version of the manuscript in order to address them.

P6332 The station at Finokalia is located 50 m far from the coast at about 250 m above sea level. However, a map is currently included in the revised version of the manuscript.

P6333 At the University campus site intensive sampling and analyses were performed through campaigns consisting of hourly measurements of 2 to 3 days per month (250 samples).

P6333 The standard mixture containing 100 ppmv of major C2-C4 hydrocarbons was supplied by Air - Liquide and it consisted of ethane (104 ppm), ethene (110 ppm), propane (104 ppm), and n-butane (100 ppm) in N<sub>2</sub>. The stated accuracy was 2%.

The identified hydrocarbons were quantified on the base of the assumption of a uniform per-carbon response (C-response) of the FID detector to the hydrocarbons of the primary calibration gas mixture (C2-C4 range). The reproducibility of the standard was better than 1% and the overall reproducibility of the analysis of the order of 2%. The detection limit was of the order of 2 to 5 pptv and the precision of the analytical technique was previously evaluated by Boissard (1992) to be within 6%. This calibration procedure has been previously described in details (Bonsang and Lambert, 1985; Boissard et al., 1996; Bonsang and Kanakidou 2001). The method is also suitable to quantify heavier NMHC, at pptv levels, and has been also validated during intercomparison exercises (Apel et al., 1994). Per-carbon response factor of an FID detector to various carbon number on per molecule basis has been used in this work for the quantification of the sampled hydrocarbons. It has been however observed that the carbon response factor for acetylene is lower (of the order of 10%) than for other hydrocarbons, for which the response per carbon is identical, and remains within the range of accuracy of the measurements (lower than 2%). Acetylene, however, is usually used for its relative variation and as a tracer of contaminated air masses transported from polluted areas.

P6334 The word diurnal has been entirely removed from the text and from the description of Fig. 1 (in the revised version of the manuscript Fig. 2).

P6334 We added a new figure (Fig. 1c) on a 24 hour clock as proposed by the reviewer to better discern the diel trend. Regarding the variation of propane, it is clear that during days with no significant change in air masses origin (as depicted by the variability in Rn222 levels) propane presents the same behaviour with the C4 and C5 alkanes. However, the diel trend of propane is not visible anymore during days with changes in the Rn222 levels, a situation which is expected when considering its longer lifetime. The increase in the hydrocarbon levels during night-time is due to the cessation of

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their chemical sink induced by the OH and Cl radicals. The night-time recovery trend could also indicate either unimportant night-time chemistry due to NO<sub>3</sub> radicals or the existence of a relatively constant source of hydrocarbons influencing the sampling location. Mega-cities like Athens, Istanbul and several others, with population more than 1-3 million of inhabitants, located upwind our sampling station can also account for such source of hydrocarbons under a constant air masses origin.

P6334 Lidar measurements performed during the campaign showed no significant changes in the marine boundary layer (MBL) during the sampling period (page 6334, lines 23-25). This behaviour is expected for a marine site as Finokalia, and long-term measurements of the BL reported by Gerasopoulos et al. (2006) confirm this assumption.

P6334 A new format is proposed for Fig.2 (in the revised version Fig. 3) in order to fulfil this requirement.

P6335 The reviewer is right and the sentence has been accordingly rephrased.

Our concept is based on the following assumption: The variation of a hydrocarbon level ( $dC/dt$ ) can be described by the following equation:  $dC/dt = P - S - Ex$ , where P represents local production, S denotes the chemical sink and Ex is the exchanges with the free troposphere. Assuming i) that the local production is equal to 0 (valid for alkanes as seawater represents a weak source for alkanes) and ii) that the Ex is very small compared to chemistry (S), as it has been shown in previous works in the area for dimethylsulfide (DMS), a VOC with a similar lifetime to C<sub>4</sub>-C<sub>6</sub> hydrocarbons, then the equation becomes:  $dC/dt = - S$

The reviewer is right with the assumption concerning the dilution and photochemistry processes. Below we are presenting several arguments indicating that dilution and mixing was unimportant and that the observed variability is mainly due to chemistry.

1.The concept of the trace-gas mixing ratio variability versus hydrocarbon lifetime has

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been investigated for the performed measurements. This concept is based on the dependence described by the equation  $\ln(X)=A \times \text{power}(t,-b)$ , where  $\ln(X)$  is the relative standard deviation of the natural logarithm of hydrocarbon mixing ratio,  $t$  is hydrocarbon atmospheric lifetime due to OH radicals mainly, and  $A$  and  $b$  are fitting parameters (Jobson et al., 1999). In order to differentiate between the importance of the photochemical processing or preponderance of the source strength in the hydrocarbon distribution patterns,  $b$  is used as a good indicator parameter. Through the performed analysis, linear relationships ( $\text{Log}(\ln(X))$  vs.  $\text{Log}(\text{hydrocarbon lifetime})$ ) were derived at each of the investigated site (natural, rural, urban) with the  $b$  factor following the order  $0.64$  (natural)  $>$   $0.37$  (rural)  $>$   $0.23$  (urban). This, indeed, suggests that at a remote site (natural assigned in our case) dynamic and source contribution play a minor role compared to the photo-chemical processing ( $b$  is approaching the value of 1) while at an urban site, under a more preponderant and consequent anthropogenic influence, the source strength becomes more important (value of parameter  $b$  shifted toward 0). The value for the rural site suggests intermediate conditions between natural and urban.

2. Dilution of the air masses can be estimated using  $\text{Rn}222$  variability measured at the marine site. As  $\text{Rn}222$  is emitted from the continents only, when travelling above seawater its concentration decreases due to both the radioactive decay and the dilution.  $\text{Rn}222$  background concentration above continents is of the order of  $100 \text{ pCi m}^{-3}$  in agreement with the value of  $120 \text{ pCi m}^{-3}$  observed during the second period of the intensive in summer 2006 (Fig. 2a), when air masses changed direction and originated from the island (western sector influence). During most of the experimental period, and under the marine sector influence, the mean  $\text{Rn}222$  activity was of the order of  $65 \text{ pCi m}^{-3}$ . Thus, dilution of air masses is given by the equation:

$$D = (\text{Rn}0/\text{Rnt}) \times e^{-k \times t}$$

where  $D$  denotes the dilution factor,  $\text{Rn}0$  is the background concentration of  $\text{Rn}222$ ,  $\text{Rnt}$  is  $\text{Rn}222$  concentration at time  $t$  in a transported air mass and  $k$  is the radioactive decay (Polian, 1984). By using observed  $\text{Rn}$  diel variability during the measuring pe-

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riod and in air masses of the same origin (based on trajectory analysis) and for  $k = 0.18$  d<sup>-1</sup>, we obtain dilution factors (D) ranging from 1.06 to 1.23 (average of  $\sim 1.16$ ). This corresponds to an average 12 hour reduction by 15% due to dilution that is low compared to the photochemical decay of C4-C6 hydrocarbons. Indeed, during the same period the decay due only to oxidation by OH radical accounts for 50-60% reduction in hydrocarbon levels, i.e. a factor of 3 to 4 larger changes than attributed to the dilution.

3. Finally, several authors (Ehhalt et al., 1998; Jobson et al., 1999; Parrish et al., 2007) suggested that, in an isolated air parcel, normally the natural logarithms of the ratios between various hydrocarbon pairs define clear linear relationships with the slope determined by the OH rate constants (predominant reaction sink pathway). Results from the analysis of the ratios between natural logarithm of various hydrocarbon pairs are also investigated and presented in Table 1 in the revised form of the manuscript. Data are compared with similar information reported by Parrish et al. (2007).

4. For example, in the present study analysis of the ratio  $\ln(\text{n-butane/ethane})$  vs.  $\ln(\text{propane/ethane})$  indicate a value of 1.61 for the rural site and 1.62 for the natural site. Parrish et al. (2007) suggest that such behaviour is expected if aging is indeed causing the observed relationships. Our observation regarding the  $\ln(\text{n-butane/ethane})/\ln(\text{propane/ethane})$  ratio agrees well with the 1.67 (a value deduced from measurements performed from 2001 to 2004) reported by Parrish et al. (2007). The theoretical kinetic data adopted in the present work suggest a much larger ratio than normally observed (2.47 that is about 37% higher than the value derived from the observations in the present study) and suggest evolvement of photochemical processing of the air mass.

5. For the  $\ln(\text{i-pentane/propane})$  vs.  $\ln(\text{n-butane/propane})$  the ratio derived from the measurements performed in the present work is 1.32 for the rural site and 1.35 for the natural site. Both ratios are about 38% lower than those predicted by the kinetic data. In addition the average ratio of 1.34 is about 45% lower than that reported by Parrish et al. (2007).

6. Based on the approach developed by Ehhalt et al. (1998), comparison of the theoretical slope with the observed one provide information on the importance of the removal by mixing with respect to the chemical decay. A value of 1 for the observed slope indicates that removal is essential due to mixing. If the two slopes are equal then transport and chemical removal are of similar importance. Finally, if the theoretical slope is greater than the observed one then the chemical decay is mostly responsible for local hydrocarbons removal. In both studied cases the third condition is fulfilled and therefore these observations clearly indicate the predominant role of chemistry. The above mentioned arguments have been added at the revised version of the manuscript.

P6336 The data presented in Fig. 3a (now Fig. 4a) are mean relative mixing ratios of selected hydrocarbons measured at Finokalia from 26 July to 4 August, 2006. In the revised manuscript, Fig. 3a (Fig. 4a) will depict averages in the relative mixing ratios of the measured hydrocarbons.

P6336 Hydroxyl radical concentrations derived from the box model are averaged monthly and for the daytime period.

P6337 “Appropriate meteorological conditions” refer to northward wind direction and wind speed higher than  $4\text{ m s}^{-1}$  to ensure that the investigated site is under the influence of chemically aged air masses. Under such conditions the applied concept for the determination of OH radicals is valid.

P6337 The missing word has been inserted in the revised manuscript.

P6337 The observation of the referee that data at high n-butane mixing ratios ( $> 1000$  pptv) display a constant ratio of about 0.4 is valid only for the rural site during winter. This can be explained mainly by a lowering in the photochemical decay of the measured hydrocarbons and thus higher influence of dilution and mixing. At the natural site, and for n-butane mixing ratios far from the detection limit (30-100 pptv) the ratio is not constant and varies by more than a factor of two. Given the high accuracy of the measurements at these levels, the results are not biased from the analytical uncer-

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tainties and the change in the *i*-butane/*n*-butane ratio is a real situation that suggests the presence of the Cl atoms, as already presented by various authors. Note that the absence of Cl chemistry would imply a constant *i*-butane/*n*-butane which could be the case during the winter time. The log(*i*-butane) vs. log(*n*-butane) distribution has been studied and a good correlation has been found. However as the reactivity of these two hydrocarbons towards OH radicals is almost the same we cannot use the concept developed by Parrish et al. (2007) or Ehhalt et al. (1998). Indeed the observed slope for the log(*i*-butane) vs. log(*n*-butane) distribution is almost 1, close to the theoretical value. This does not allow to distinguish between chemistry and dilution (see above) and thus is not presented in the manuscript because is not informative. This ratio is used in the manuscript qualitatively only and in order to compare the results with earlier performed studies that report the existence of the Cl atoms.

P6337 Both points have been already addressed. As we mentioned above the log(*i*-butane) vs. log(*n*-butane) distribution has been studied only for qualitative purposes. The observed slope for the log(*i*-butane) vs. log(*n*-butane) distribution is almost 1, close to the theoretical predicted value. This does not allow to distinguish between the role of chemistry and dilution (see above) and thus is not presented in the manuscript because is not informative. During the low insolation period (mainly winter time) the photochemical decay of the hydrocarbons is very low and thus the influence from dilution and mixing is much higher.

P6338 This point has been also addressed in previous sections. In particular, the impact of mixing has been discussed under point 7 based on Rn222 observations.

P6339 Experimental error, uncertainties both in the OH estimates and available rate constants account for the large standard deviations of the calculated Cl concentrations.

P6340 Carbon monoxide (CO) has been selected for this estimate also for qualitatively comparison with previous works (Singh et al., 1996) as at the natural site, where the background monitoring station is (Finokalia), a CO Analyser (Thermo Electron 48C) is

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used for the continuous monitoring of the CO level.

Table 3 The authors apologise for not including Atkinson and Aschmann (1985) reference in the original text. Indeed the  $1.5 \times 10^{-11}$  value given by Atkinson and Aschmann (1985) is much larger than the  $4.0 \times 10^{-12}$  cm<sup>3</sup> molec<sup>-1</sup> s<sup>-1</sup> reported by Wallington et al. (1988).

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