

C₇-C₁₁ aromatic and n-alkane hydrocarbons measured by a comprehensive gas chromatography (GCxGC) system during the MINOS Campaign

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1. Introduction

Increased anthropogenic emissions of non-methane hydrocarbons (NMHCs) causes deterioration of air quality and alteration of air composition and properties. Atmospheric NMHCs, especially alkanes and aromatics, are mainly removed by reactions with OH. The degradation reactions of NMHCs can lead to the formation of O₃ and other compounds, and thereby can influence the distribution and budget of tropospheric OH.

A common method for measuring ambient NMHCs is gas chromatography (GC). However, the separation power of conventional GC is inadequate to simultaneously measure a large number of compounds. This problem can be solved by the novel comprehensive two-dimensional gas chromatography (GCxGC) technique. Here we present (GCxGC) measurements of some hydrocarbons. Details about the instrumental set-up as well as the identification and quantification are given in a separate paper presented at this conference (Xu et al., 2002)

2. Experimental

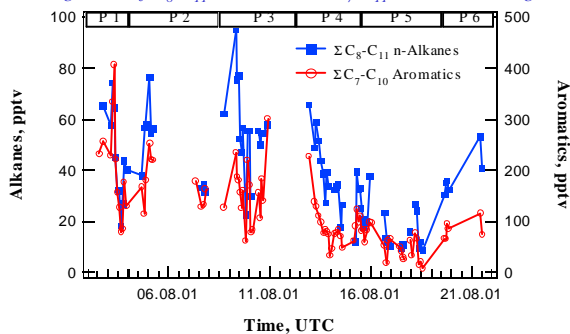
Site: In situ measurements were performed during the Mediterranean Intensive Oxidant Study (MINOS) campaign in August 2001 at the Finokalia ground station (35°19' N, 25°40' E, 130 m asl) established by the University of Crete. Crete is located in the middle of the Eastern Mediterranean, about 400 to 1000 km away from the coasts of Greece and Turkey. The mesoscale wind was steady and northerly throughout the campaign. The windspeed averaged 11.7 m s⁻¹, corresponding to a half to one day transport time from continental sources to measurement point. Local sources were not significant.

Sampling and Analysis: A thermal desorber-GCxGC-FID system was used for the on-line sampling and measurement of atmospheric trace gases (see Xu et al. (2002) for details). The sampling height was about 7 m above the ground. The precision is estimated to be 5-28%, based on the field calibrations. The systematic error was about 5%. Depending on compounds, the (3σ) detection limit was 3-52 pptv and 0.4-18 pptv for the first and second half of the campaign, respectively.

3. Results

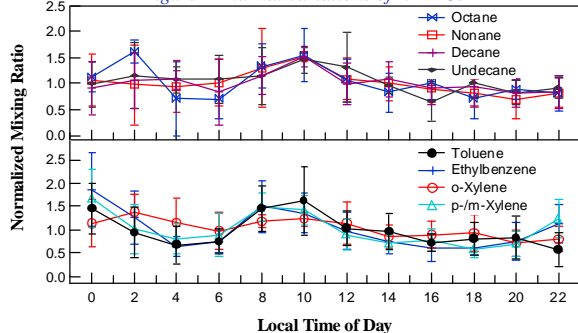
Overview: Fig.1 shows the summed mixing ratios of C₈-C₁₁ n-alkanes and C₇-C₁₁ aromatics during the whole campaign. General trends of the two quantities are similar as well as those of individual species, showing higher levels at the beginning and in the middle and lower levels in the last week of the campaign. Various air masses were encountered (P1-P6 in Fig. 1, see Salisbury et al. (2002) for details), however, changes in hydrocarbon abundances could not be explained by corresponding air mass changes alone. The low concentrations observed between 14.8.01 and 20.8.01 coincided with slightly enhanced levels of OH by about 20% (Berresheim et al., 2002).

Fig. 1 Mixing ratios of C₈-C₁₁ n-alkanes and C₇-C₁₁ aromatics during MINOS



Diurnal Variation: Mean diurnal variations shown in Fig.2 were observed in the hydrocarbon mixing ratios. Except for some slight differences, general features of the diurnal profiles for different species are consistent, showing high values in the local midnight and later morning and lower values in the early morning and evening.

Figure 2 Diurnal variations of NMHCs



Hydrocarbon-OH Relationship: In a reaction chamber, the variation of hydrocarbon C can be described by $\ln[C]/[C]_0 = -k[OH]t$, with k being the rate coefficient for the C + OH reaction. This relationship is often used to measure k under laboratory conditions. In the atmosphere, the lifetime and abundance of C depend both on the source of C and on the OH abundance. If the source is stable, a negative correlation between $\ln[C]$ and $k[OH]t$ can be expected. Indeed such correlation was observed during MINOS, as shown in Fig. 3. Since the x-axis of Fig. 3 is the integral of OH over the past 24 hours before the hydrocarbon measurement, the slope of the regression line can be treated as a fitted k . A comparison of fitted k values with literature k values is shown in Fig. 4 for a dozen compounds. For most compounds, the fitted k values are closed to the literature ones.

Fig. 3 Correlation between $\ln[o\text{-xylene}]$ and daily integral of OH

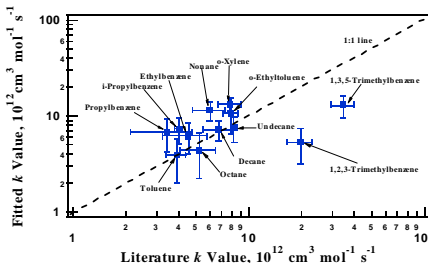
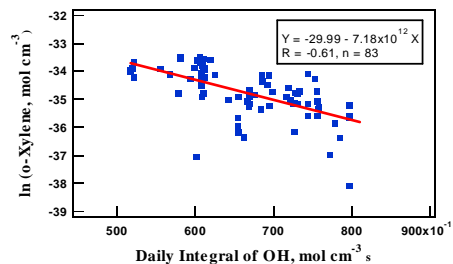
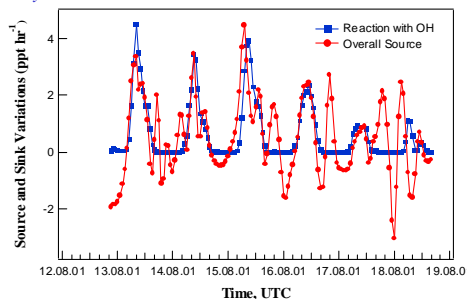


Fig. 4 Comparison of fitted k values with literature k values

Source and Sink Variations: The correlation shown in Fig. 3 only accounts for a small fraction (37%) of the variance of $\ln[o\text{-xylene}]$. The remainder can be attributed to the variation in the source strength. Fig. 5 gives an example of the

Fig. 5 Variation of the overall source and sink of ethylbenzene

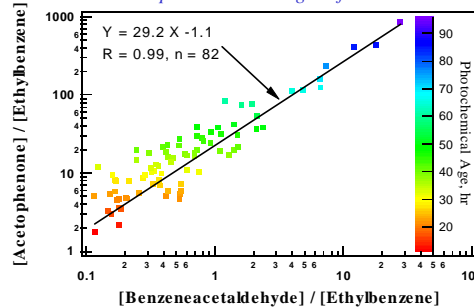


variation, showing the relative fluctuations of the overall source ($\equiv \Delta[C]/\Delta t + k[OH][C]$, can be negative) and the chemical sink of ethylbenzene during the period from 13.8.01 to 19.8.01. While the loss of ethylbenzene due to the reaction with OH shows usually one peak within a day, the overall source peaks 2 or 3 times.

[Product]/[Precursor] Ratio and Photochemical Age: Simultaneous measurements of NMHCs and their degradation products allow an application of the sequential reaction model (Bertman et al., 1995). Two of the products from the ethylbenzene + OH reaction are acetophenone and benzeneacetaldehyde, which are decomposed in subsequent reactions.

Fig. 6 compares the ratios of both products to their precursor. An excellent correlation exists between both ratios. Photochemical ages of air masses have been estimated based on the literature rate constants for the reactions of ethylbenzene and acetophenone with OH and the average OH abundance during the campaign. The ages ranged from 10 to 95 hours.

Fig. 6 Correlation between [product]/[precursor] ratios and the photochemical ages of air masses



4. Conclusions

Atmospheric VOCs at Finokalia, Crete, were measured during MINOS using the novel GCxGC technique. Mixing ratios of C₇-C₁₁ hydrocarbons were in the pptv to sub-pptv range, showing significant day-to-day and diurnal variations. The variations were caused partially by changes in the OH abundance, but to a larger extent by the unstable hydrocarbon sources. In spite of the unstable sources, the fitted k values are comparable to the literature ones. There is an excellent correlation between $[\text{acetophenone}]/[\text{ethylbenzene}]$ and $[\text{benzeneacetaldehyde}]/[\text{ethylbenzene}]$, agreeing with the prediction of the sequential reaction model. The estimated photochemical ages of air masses lie in the range of 0.5-4 days.