Atmospheric Chemistry and Physics
An Interactive Open Access Journal of the European Geosciences Union

Atmos. Chem. Phys., 3, 1461-1475, 2003
www.atmos-chem-phys.net/3/1461/2003/

GC×GC measurements of C_7-C_{11} aromatic and n-alkane hydrocarbons on Crete, in air from Eastern Europe during the MINOS campaign

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Abstract. During the Mediterranean Intensive Oxidant Study (MINOS) campaign in August 2001 gas-phase organic compounds were measured using comprehensive two-dimensional gas chromatography (GCxGC) at the Finokalia ground station, Crete. In this paper, C_7-C_{11} aromatic and n-alkane measurements are presented and interpreted. The mean mixing ratios of the hydrocarbons varied from 1±1 pptv (i-propylbenzene) to 43±36 pptv (toluene). The observed mixing ratios showed strong day-to-day variations and generally higher levels during the first half of the campaign. Mean diel profiles showed maxima at local midnight and late morning, and minima in the early morning and evening. Results from analysis using a simplified box model suggest that both the chemical sink (i.e. reaction with OH) and the variability of source strengths were the causes of the observed variations in hydrocarbon mixing ratios. The logarithms of hydrocarbon concentrations were negatively correlated with the OH concentrations integral over a day prior to the hydrocarbon measurements. Slopes of the regression lines derived from these correlations for different compounds are compared with literature rate constants for their reactions with OH. The slopes for most compounds agree reasonably well with the literature rate constants. A sequential reaction model has been applied to the interpretation of the relationship between ethylbenzene and two of its potential products, i.e. acetophenone and benzeneacetaldehyde. The model can explain the good correlation observed between [acetophenone]/[ethylbenzene] and [benzeneacetaldehyde]/[ethylbenzene]. The model results and field measurements suggest that the reactivity of benzeneacetaldehyde may lie between those of acetophenone and ethylbenzene and that the ratio between yields of acetophenone and benzeneacetaldehyde may be up to 28:1. Photochemical ages of trace gases sampled at Finokalia during the campaign are estimated using the sequential reaction model and related data. They lie in the range of about 0.5-2.5 days.

Final Revised Paper (PDF, 352 KB) Discussion Paper (ACPD)

Citation: Xu, X., Williams, C., Plass-Dülmer, H., Berresheim, H., Salisbury, G., Lange, L., and Lelieveld, J.: GC×GC measurements of C_7-C_{11} aromatic and n-alkane hydrocarbons on Crete, in air from Eastern Europe during the MINOS campaign, Atmos. Chem. Phys., 3, 1461-1475,

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