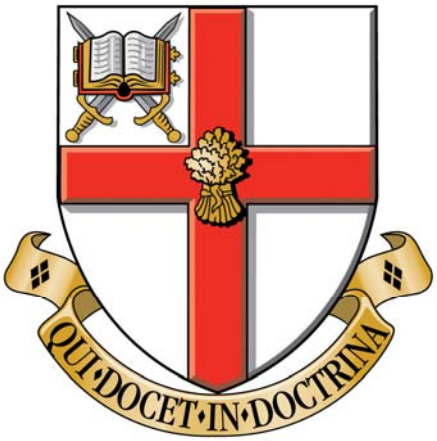

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Volatile organic compounds (VOCs) in photochemically aged air from the Eastern and Western Mediterranean

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In summer 2014 a comprehensively instrumented measurement campaign (CYPHEX) was conducted in northwest Cyprus in order to investigate atmospheric oxidation chemistry in the Mediterranean region. The site was periodically influenced by the northerly Etesian winds advecting air from Eastern Europe (Turkey and Greece) and from westerly winds bringing more photochemically processed emissions from Western Europe (Spain and France). In this study the data from a Proton Transfer Reaction Time of Flight Mass Spectrometer (PTR-TOF-MS) are analyzed.

Generally, oxidized volatile organic compounds (OVOCs) such as methanol and acetone were measured in high mixing ratios (max. 9.5 ppb, min. 1.3 ppb, average 3.2 ppb for methanol, max. 7.9 ppb, min. 1.3 ppb, average 2.4 ppb for acetone) while precursors like propane showed low values (max. 500 ppt). This demonstrates that the air measured was oxidized to a high degree over the Mediterranean Sea. Low values of acetonitrile throughout the campaign indicated no significant influence of biomass burning on the data. Temporal variations in VOC mixing ratios and precursor/product ratios over the campaign can be explained by using the HYSPLIT backward trajectory model which delineated air masses originating from Eastern and Western Europe. Diel variations of reactive VOCs such as isoprene and terpenes were also observed at the site. A sharp increase in isoprene and monoterpenes at circa 9:00 local time indicated that the 600 m hilltop site was influenced by ascending boundary layer air at this time.

In this study, particular emphasis is placed on acetic (ethanoic) acid measured by PTR- TOF-MS and calibrated by a permeation source. Acetic acid is an atmospheric oxidation product of multiple volatile organic compounds, emitted directly from vegetation, and found in abundance in the Mediterranean region (max. 2.7 ppb, min. 0.2 ppb, average 0.8 ppb). Acetic acid contributes to the acidity of precipitation in remote areas, can be incorporated into aerosols by adsorption on the surface and thereby alter the activity due to their high polarity. Correlations of acetic acid with peracetic acid, humidity and ozone have been investigated in order to better understand the sources influencing acetic acid at the site and to assess its potential as a marker for Criegee radical chemistry.