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Title of project:

Free Troposphere Experiment 2003 (FREETEX)

Project leader and team

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Project description:

C₂-C₅ alkanes, alkenes and alkynes are useful tracers of natural and anthropogenic emissions. With diverse emission sources and moderately short atmospheric lifetimes, non-methane hydrocarbons (NMHCs) exhibit significant latitudinal, seasonal and vertical gradients [1]. They primarily react with the hydroxyl (OH) radical in the atmosphere, although also with ozone, nitrate, chlorine and bromine. Unsaturated NMHCs (alkenes) react faster with OH compared to the saturated alkanes, and therefore, in remote atmospheres (e.g. marine boundary layer, or free troposphere), long-lived alkanes such as ethane and propane are generally the most abundant [1]. Observing the changing ratios in abundance particular hydrocarbons, e.g. branched to straight chain alkanes, alkanes to acetylene etc – can give an indirect measurement of the integrated radical concentration, and this property has been used to probe not only OH [2] but also NO₃ [3], Cl and Br [4] in the atmosphere. These unique reaction rates provide information on transport and dilution of air-masses, but are needed also to understand the photochemical processes occurring *in situ*, as NMHCs, along with NO_x, are the key chemical precursors of O₃ [5]. In the free troposphere where O₃ has an enhanced photochemical lifetime and a proportionally greater influence on climate [6], light hydrocarbon measurements are needed to calculate free tropospheric photochemical O₃ production, and in determining their potential to act as sinks for OH.

PAN, a major component of photochemical smog, also plays an important role in the chemistry of the free troposphere and in photochemical O₃ cycles. PAN is a secondary pollutant, formed when hydrocarbons are oxidised in the presence of NO_x [7]. An important feature of PAN is that it is thermally unstable and, therefore, its atmospheric lifetime is strongly dependent on the ambient temperature. In the cold free troposphere the PAN molecule may persist for several months [7] and may be transported over long distances before decomposing when an airmass subsides to release NO_x [8]. By this mechanism, PAN can have a profound effect on both regional and global oxidant budgets.

The PAN GC and NMHC GC, (Organics by near Real time Airborne Chromatograph – ORAC) have been designed to make both ground and aircraft measurements. To meet aircraft specifications, both instruments have been designed to be entirely self-contained and have low weight and power consumption. The two instruments are particularly robust and are able to withstand up to 9g of force. As part of the 2003

project we have made the first low atmospheric pressure tests for these instruments in addition to providing an opportunity to establish sensitivity and response performance in cold, dry and clean free tropospheric air.

This project also provided the opportunity for the first field-test of a new automated peroxides instrument, in preparation for its participation in a project in Antarctica. The instrument ran continuously for 14 days and allowed problems to be identified that could be rectified in advance of its deployment in Antarctica.

A time-series showing propene and CO data from the second half of the measurement campaign is presented in Figure 1. Both compounds exhibit a diurnal cycle, displaying a minimum in the early morning hours and a maximum around midday. The maximum observed in CO on the 6th March occurs later in the evening - this shift may be due to a change in the air mass sampled, as the trajectories show a change in direction from NW to SW. Such diurnal cycling may be a function of changing boundary-layer height. Mountain research stations, such as the JFJ, tend to reside in the FT at night as the boundary layer height (BLH) decreases due to reduced temperatures. In the daylight hours, the boundary layer increases, allowing emissions from the alpine valleys to be sampled, thus, leading to increased levels of anthropogenic compounds, such as CO and propene, measured during the day. Such pronounced diurnal cycles were not observed in the alkane data, since these species are more abundant in the FT, therefore, changes in the boundary layer height may affect the ambient levels to a lesser degree.

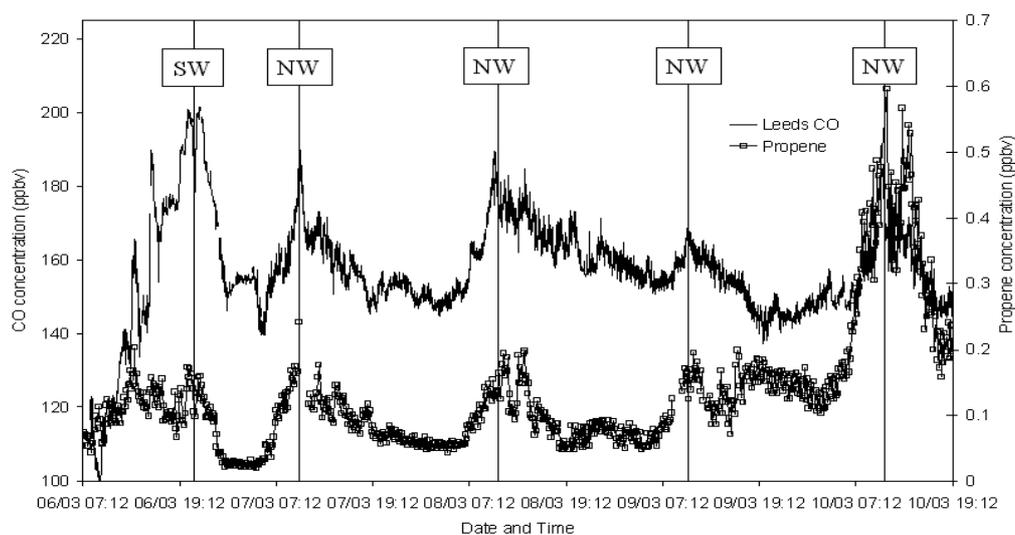


Figure 1 Time-series of propene and CO. CO daily maximum displayed.

Of the species measured by ORAC and the EMPA GC-MS only *n* & *iso*-butane were common to both instruments. The datasets agreed well throughout the campaign for *iso*-butane, with mean concentrations of 0.076 ppbV and 0.077 ppbV by the EMPA GC and ORAC respectively. There were, however, significant differences in the *n*-butane concentration, highlighted in particular when the butane ratios are calculated. A butane ratio of 1:2 has previously been reported at the JFJ by Carpenter *et al* [12] and this is recreated by the EMPA instrument. A much higher ratio observed at times by ORAC may be due to a co-eluting compound, possibly a halocarbon.

Peroxyacetyl nitrate data collected throughout the campaign is presented in Figure 2. The mean PAN concentration was calculated to be 0.142 ppbV, however, at times falling as low as 0.011 ppbV. Plotted alongside O₃ and CO, PAN exhibits both positive and negative correlations with respect to O₃ and a general positive trend with CO. Since both O₃ and PAN are secondary pollutants polluted air masses would be expected to have a positive correlation. A negative correlation is likely to be observed when the polluted air mass has undergone O₃ titration with NO, or when an air mass has a stratospheric influence.

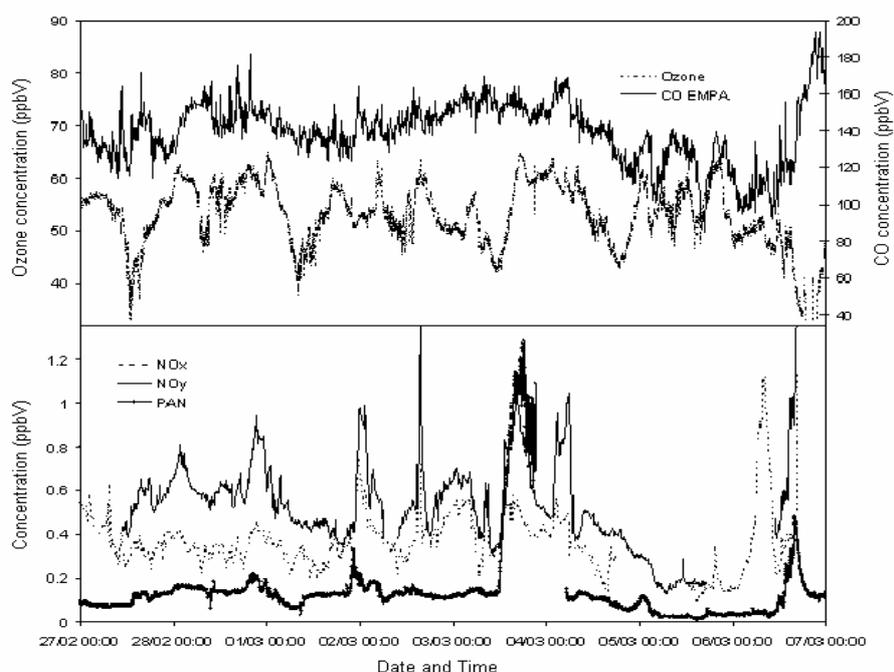


Figure 2 Time-series of CO and O₃, PAN, NO_x and NO_y

PAN has also been compared to NO_x and NO_y data during this campaign (Figure 2). PAN has previously been reported to contribute up to 36 % of the NO_y seen at the JFJ station [12, 13], however PAN contributions as low as 19 % during autumn and winter months have been reported [11]. The mean contribution throughout this campaign was calculated to be 21 %. This low PAN contribution is due to proportionally higher NO_x levels, calculated to contribute an average of up to 70 % of the NO_y during this campaign. This is a much larger contribution than previously reported [14] and indicates that the JFJ was influenced by polluted air masses for the majority of the measurement period.

Hydrogen peroxide was observed in the sub-ppbV range, as shown in Figure 2. Methyl hydroperoxide (MHP) was also observed but data has yet to be processed to obtain concentration values, which are considerably lower than those of H₂O₂.

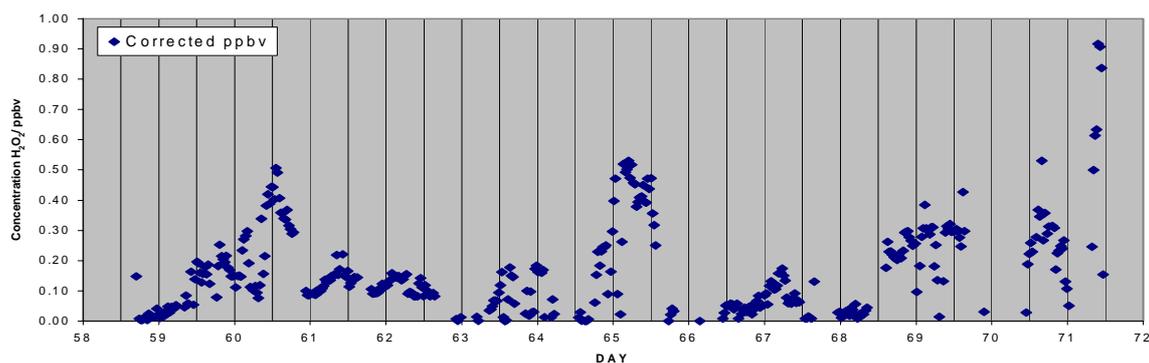


Figure 3: Time Series of [H₂O₂] at JFJ for 27/02/03 (Day 58) to 12/03/03 (Day 72)

Figure 3 shows that there are two distinct periods of higher H₂O₂ concentration occurring during Julian day 60 (01/03/03) and 65 (06/03/03). Initial analysis indicates that these periods appear to correspond to a change in local wind direction change, from a general north-westerly direction (270-360°) to a south-easterly direction (90-180°), and to increased pressure and low NO_x regimes. This implies that air masses being transported locally from the north-west generally show a *lower* peroxide (or peroxide pre-cursors) concentration than air masses transported from the south-east. Furthermore, it suggests that air masses moving from the south-east have increased photochemical activity to those from the north-west, over this period. A third, less well-defined period of higher H₂O₂ concentration occurring during days 68-71 (09-12/03/03) does not correspond to a change in local wind direction.

Periods of very low H₂O₂ concentration appear to correspond with periods where NO concentrations exceed 0.1 ppb, which is consistent with the scavenging of HO₂ radicals by NO thereby suppressing H₂O₂ formation. Diurnal cycles can also be seen in Figure 3, being especially well-defined during days 61 and 62 (02 and 03/03/03 respectively). Further analysis of this dataset alongside others collected at the observatory is presently being undertaken in order to establish the reasons for the observed peroxide variation.

Throughout the measurement period the PAN, NMHC and H₂O₂ observations highlighted specific chemical changes to airmass composition that occur as a function of meteorological transport. Coupled with back trajectory analysis, the levels of the trace gases can be qualitatively described by examining the airmass origin. In terms of their capacity to measure both PAN and NMHCs at high altitudes and specifically the free troposphere, the GC techniques reported here have proved successful. The new automated instrument for the measurements of H₂O₂ and ROOH was also successful, any problems were identified and rectified and the instrument is currently deployed in the Antarctic.

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Key words:

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Internet data bases:

http://www-users.york.ac.uk/~chem89/Intro_group.htm

<http://www.env.leeds.ac.uk/research/ias/index.htm>

Scientific publications and public outreach 2003:

Refereed journal articles

Whalley, L. K., A.C. Lewis, J.B. McQuaid, R.M. Purvis, J.D. Lee, K. Stemmler, C. Zellweger, and P. Ridgeon, Two High-speed, Portable GC Systems Designed for the Measurement of Non-methane Hydrocarbons and PAN: Results from the Jungfraujoch High Altitude Observatory, accepted *Journal of Environmental Monitoring*, 2003

Thesis

Purvis, R. M., Transport and distribution of non methane hydrocarbons in the free troposphere over Europe, PhD Thesis, University of Leeds, 2003 (FREETEX 2001 and 2002)

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