

Name of research institute or organization:

Department of Chemistry, University of Leeds

Title of project:

Free Tropospheric Experiment 2002 (FREETEX 02): Study of non-methane hydrocarbons in the free troposphere using gas chromatography

Project leader and team:

Dr Alastair Lewis, project leader
Dr James Hopkins, Katie Read, Ruth Purvis

Project description:

Introduction: The fourth FREETEX (**Free Troposphere Experiment 02**) campaign took place between 4th and 24th January 2002 at the Jungfrauoch High Alpine Research Station, Switzerland at 3580m (7.98°, 46.55°), with previous campaigns at this site proving to be successful. {Zanis, 2000 #88;Zanis, 1999 #86;Zanis, 1999 #87;Forrer, 2000 #85} The main objectives of this experiment were to increase our understanding of the role of reactive non-methane hydrocarbons (NMHCs) in the lower free troposphere and their influence on tropospheric ozone and to implement and test the performance of the new and improved instrument under these extreme conditions as preparation for an Antarctic Campaign.

Experimental: The Jungfrauoch High Alpine Research Station is an ideal site to investigate background concentrations of NMHCs in the free troposphere. There are little local pollution sources to influence results and so the majority of species seen which may have an impact on the ozone concentrations are due to long-range transport. In addition the minimum temperature of -20°C at this time of year and lower atmospheric pressure conditions due to the high altitude provide an ideal test bed for the Antarctic. Sampling was via a heated inlet, through a 3.1m long, 8cm ID stainless steel tube to a shared glass manifold. A metal bellows pump pulled the air through 5 m of 1/8" stainless steel tubing and pushed it into a Gas Chromatograph with Flame Ionisation detection (GC-FID). 1 litre samples were taken hourly using a dual carbon sorbent trapping technique and a total of 26 C₂-C₈ non-methane hydrocarbons were detected and measured. For the first time, air was used as the drying gas through the nafion to dry the sample flow and a completely automated valve system was implemented for the sampling, blanks and calibration.

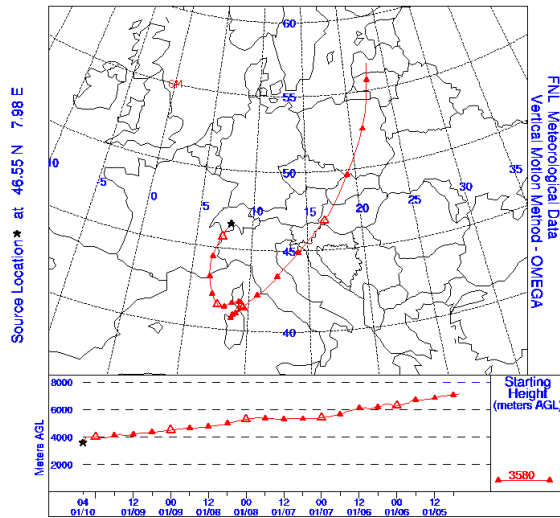
Results: It is common in hydrocarbon analysis to run a 5-day back trajectory analysis to determine a possible source, as this considers the lifetimes for most of the observed compounds. The analysis was done at intervals of 4 hours using the vertical motion method, which uses the meteorological model's vertical velocity fields. Four types of air mass can be used to classify the air arriving during the experimental period.

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Activity Report 2002

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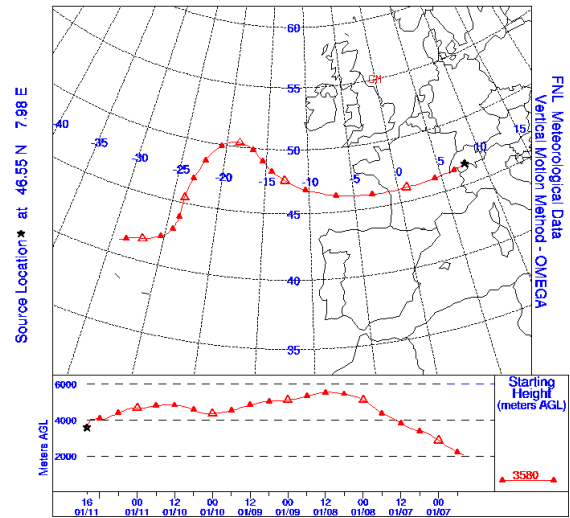
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Backward Trajectory Ending- 04 UTC 10 JAN 02



A. Southerly Anticyclonic

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Backward Trajectory Ending- 16 UTC 11 JAN 02

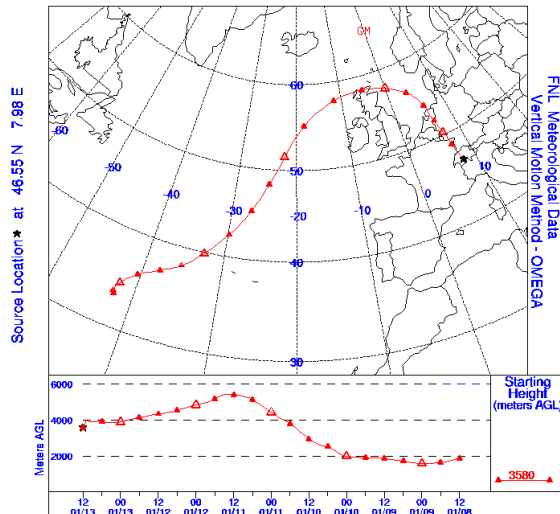


B. Westerly

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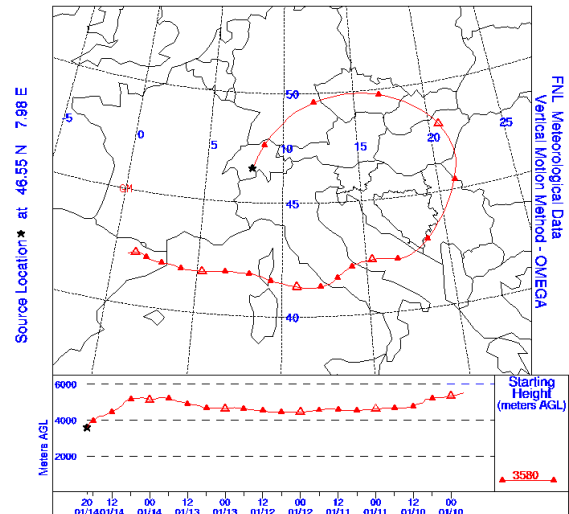
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C. North-Westerly

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Backward Trajectory Ending- 20 UTC 14 JAN 02



D. North-Easterly Cyclonic

Southerly Anticyclonic (A): The Southerly Anticyclonic air was seen from JD 8.50 to JD 11.70, the start of the campaign and then again from JD 22.00 to JD 22.33 at the end. It is “Anticyclonic” because the air mass travels in a clockwise direction before arrival at the sampling point. The classification of the air mass is only based on the previous 24 hours although 5-day back trajectories have been calculated and observations show that in this time-span the origin of the air ranges from polar areas to Europe and even to North America. Southerly air will approach the Jungfraujoch Station over the Aletsch glacier, and is one of the predominant winds to this site. This airmass has continental influences; it originates over Europe and spends the 5 days prior to sampling there, contaminated by hydrocarbons with lifetimes of a few days. This air is therefore the most polluted of the campaign showing levels of between 114 pptv and 335 pptv for n-butane. Ethene and propene and 1, 3-butadiene have maximums of 490 pptv, 174 pptv and 17.5 pptv respectively (figure 1). However with respect to short-lived alkenes such as these if the pollution levels are high then the few hours prior to sampling provide more information than the origin of the air over the previous 5 days. Considering the height at which we were at, these levels were likely due to a very local source, maybe from smoking pollution. There is a period towards the end of this air-mass JD 11.62-12.22 and also at some times during the westerly (B) (JD13.24-13.81), that the O₃ drops out with the CO and hydrocarbons (figure 3) which would indicate a well processed air-mass with no stratospheric influence, for example one with a maritime history, and indeed this mainly ascending air does have an oceanic background.

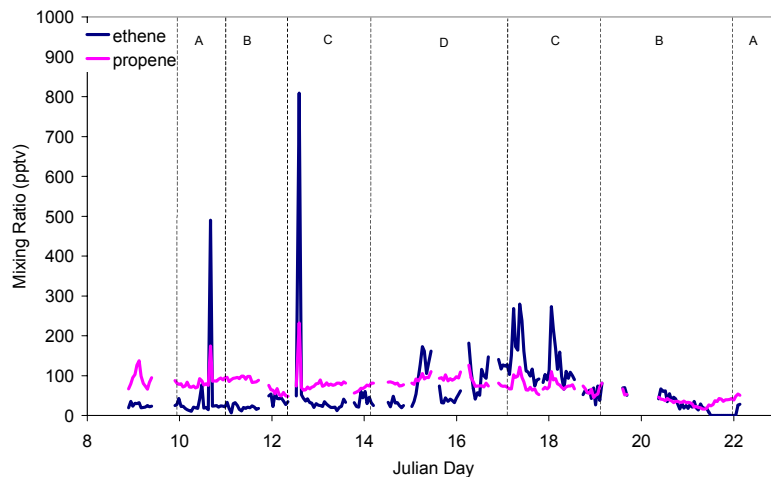


Figure 1: Time-series of ethene and propene.

Westerly (B): Although the last 24 hours classifies these days as westerly, there are clearly 2 distinct types of air mass. The air sampled JD 11.17 to JD 12.33 originates in the sub-tropical Atlantic Ocean and the second, from JD 19.17 to JD 22.00, was in North America during the previous 5 days to sampling, and some of the trajectories show it was as recent as 2 days before. There appears to be some long-range transport occurring during this time, as it is more polluted than the earlier westerly air mass. JD 12.00 to JD 12.17 spends some time over Great Britain but this doesn't seem to affect the pollution levels. Elevated pollution levels of 455 pptv, 211 pptv, 2877 pptv, 1542 pptv are seen for n-butane, iso-butane, ethane and propane respectively between JD 20.17 to JD 20.67 which is possibly due to the air ascending from North America over the Atlantic Ocean to Jungfraujoch in Switzerland. This is the air-mass classification for the majority of the campaign.

North-Westerly (C): The air arriving at Jungfraujoch JD 12.33 to JD 14.17 and then from JD 17.17 to JD 19.17 was given a north-westerly classification. This is similar to the Westerly air mass in that it also originates in the sub-tropical Atlantic but instead of passing over France chooses Great Britain before arriving at Jungfraujoch from the north. This is a common wind direction due to the effect of the NE-SW alpine ridge on which the station is situated, creating a channelling effect. During JD 13.83 to JD 14.00 the air shows elevated concentrations of iso- and n-butane, iso- and n-pentane (figure 2), and acetylene with maximums being 166 pptv, 300 pptv, 167 pptv, 84.7 pptv, and 427 pptv, respectively. This air is of oceanic origin as before but has a local wind direction from the north-east which brings it over Norway and Sweden before arriving in Switzerland. These elevated levels may possibly be due to the fuel oil used to power the ferries across the Baltic Sea and or the fishing trawlers for the enormous fishing industry in these Scandinavian countries. It ascends originally but then descends to Jungfraujoch perhaps bringing ozone from the stratosphere which would account for the increased levels we see from JD 18.44 to JD 19.34 (figure 3), but this could also be due to long-range transport of hydrocarbons. During JD 17.17 to JD 19.17 the air again had a 5-day back trajectory extending into the sub-tropical Atlantic. For the first half of this period the air passes over France and then rises north to give the northwesterly classification. In the second half it rises earlier to pass again over Great Britain. Some of this air has a back trajectory to North America so is again fairly polluted. The back trajectory of the air arriving on JD 17.92 to JD 18.00 has a polar influence as it travels over Iceland 3 days previous to sampling.

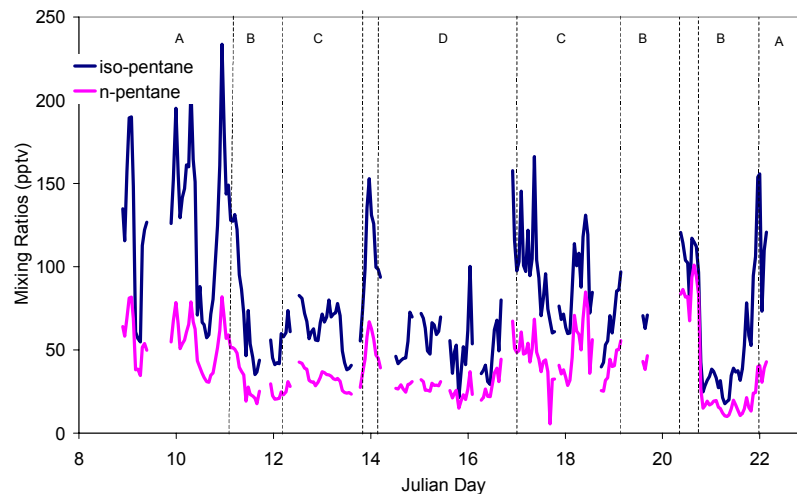


Figure 2: Time-series of iso- and n-pentane

North-Easterly Cyclonic (D): This is a very distinctive air mass and occurs from the back trajectories of JD 14.17 to JD 17.17. It is “Cyclonic”, hence the air travels in an anti-clockwise direction before arrival at Jungfraujoch. The air is from the east and has spent 5 days over continental Europe however; it is generally very clean due to it descending. The air for JD 16.00 to JD 16.17 has a 5-day back trajectory in Great Britain, JD 16.92 is very cyclonic and JD 17.00 originates in Iceland and therefore has a polar influence. During periods of “clean” air, when the airmass was descending in a cyclonic way from the northeast (D), the CO mixing ratios dropped to its lowest values of 100 ppbv whilst the ozone remained at 50 ppbv. This can be taken as a background concentration for ozone in the free troposphere in this area.

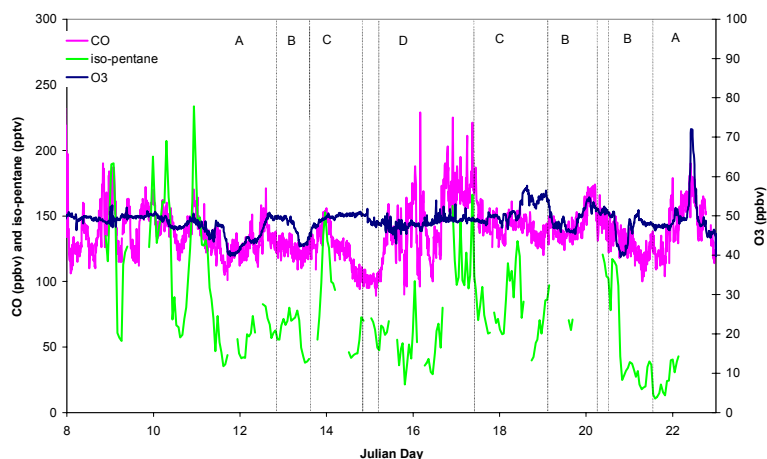


Figure 3: Time series of ozone, carbon monoxide and iso-pentane.

Conclusions: The instrument ran continuously through the campaign to allow a thorough testing of the new drying technique and automated valve system. Automated air samples, zeros, blanks, and calibration standards were run successfully and the air was dried to a dew point of -10°C . The campaign provided an opportunity to experiment with various interpretation techniques, for example, the use of back trajectory analysis. This particular dataset has been classified into four air types, which has enabled possible explanations for what was observed. As illustrated, long-range transport from a wide range of sources, has led to higher concentrations than would be expected for this region of the atmosphere and so the monitoring of NMHCs in the troposphere continues to be of major interest especially with respect to their role in tropospheric ozone production.

Key words:

Free Troposphere, non-methane hydrocarbons, ozone, gas chromatography, air analysis

Internet data bases:

<http://www.chem.leeds.ac.uk/Atmospheric/Field/field.html>

Collaborating partners/networks:

No published papers as yet

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