Name of research institute or organization:

University of Leicester

Title of project:

Composition Control in the Lower Free Troposphere

Project leader and team:

Dr. Paul S. Monks, project leader
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Project description:

Long-range transport of pollutants throughout the atmosphere and its consequences underlies many environmental problems that have arisen over the last 50 years. There are still quite large uncertainties in the budget of free troposphere trace gases. The importance of ozone and it's precursors in the free troposphere is now well established. However, the issue of the transport of anthropogenic pollutants from continental outflow and their potential coupling the natural cycles of the remote free troposphere is an issue of continuing concern. During the summer of 2005 the University of Leicester carried out a significant measurement effort at the high-altitude research station Jungfraujoch, aimed at investigating the control of composition and the effect of long-range transport (LRT) on free tropospheric chemistry. The combination of measurements provides an unique insight into LRT and lower free tropospheric chemistry.

There has been significant progress over the last decade in the measurement of a variety of chemical species that control ozone, an integral component in the control of the oxidising ability of the troposphere and a key climate gas. According to photochemical theory, the relative importance of ozone production and loss processes in the background troposphere is highly sensitive to competition between reaction of peroxy radicals with NO and the cross- or self-reactions of the peroxy radicals, and therefore the local NO_x and peroxy radical concentrations. The presence of peroxy radicals (HO_2 and RO_2) leads to net ozone production in the presence of NO_x (NO and NO_2) by allowing oxidation of NO to NO_2 without the consumption of ozone. The local ozone production $P(O_3)$ is proportional to the product of the local NO and peroxy radical concentrations while hydroperoxy radicals (HO_2) are also involved in the local destruction of ozone through the reaction between HO_2+O_3. In the very dry and cold conditions of the free troposphere this loss term can be dominant because the direct loss by photolysis of ozone and reaction of O^1D with water vapour is getting smaller. Hence, peroxy radical measurements are essential in order to provide further insight into the fast photochemistry that controls tropospheric ozone production and loss.

The aims of the experiment were by way of peroxy radical and supporting measurements,

1. To investigate the role of *in-situ* photochemistry in the control of lower free tropospheric composition in summer
2. To assess European export and transatlantic import *via* long-range transport, using trajectory analysis over the Swiss Alps
3. To quantify transport from pollutant sources in Swiss plateau and Po valley to the lower free troposphere.

4. To test and develop instrumentation used for aircraft-based studies

The University of Leicester team deployed

a) A four-channel peroxy radical chemical amplifier for the determination of $HO_2+\Sigma RO_2$ and ΣRO_2 [1].
b) Photolysis rate measurements using a diode-array based spectral radiometer [2].

The measurements from ETHZ include: NO, NO_2, NO_y, CO, O_3 and six selected volatile hydrocarbons: Routine high quality measurements of a range of trace species provided by EMPA. Measurements of PAN, formaldehyde and other volatile oxygenated hydrocarbons from 2 PhD students of ETHZ, one working at EMPA.

In the course of the experiment the University of Leicester succesfully made high quality measurements of the sum of peroxy radicals ($HO_2+\Sigma_i R_i O_2$) and a range of photolysis rates. These, in addition to the measurements made by ETH and EMPA, shall be used to provide an unique insight into the control of the chemistry and the impact of long range transport over Europe during Summer. A significant data set has been collected and analysis of the data is ongoing, leading to publication of a scientific paper in a high impact journal.

References

[1] Salisbury, G., P.S. Monks, S. Bauguitte, B.J. Bandy and S.A. Penkett, *J.Atmos.Chem.*, **41**, 163-187, 2002.

[2] Edwards, G.D. & Monks, P.S., *J.Geophys.Res*., **108**, 8546, 10.1029/2002JD002844, 2003.

Key words:

Peroxy Radicals, Troposphere, Ozone production, Composition control

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