Name of research institute or organization:

Institute for Atmospheric and Climate Science, ETH Zurich (IACETH)

Title of project:

NOy at the interface of planetary boundary layer and the free troposphere from measurements at Jungfraujoch (trace gas measurements at Jungfraujoch)

Project leader and team:

Prof. Johannes Staehelin, Project leader
Shubha Pandey, Uwe Weers

Project description:

1. Scientific background and goals of the project

NO_y is the abbreviation of a family of tropospheric trace constituents containing nitrogen in oxidized form including nitrogen oxides (NO_x: $NO+NO_2$, being important primary pollutants mainly emitted by fossil fuel combustion (in the northern midlatitudes)) plus compounds formed by oxidation of nitrogen oxides in the troposphere (including Peroxyacetylnitrate (PAN), nitric acid (HNO_3), particluate nitrates and some others). NO_x are important precursors for the formation of ozone (O_3), which is a key precursor of summer smog and an important greenhouse gas. PAN acts as an imporatnt reservoir species in tropospheric chemistry:

$$CH_3CO\text{-}O_2 + NO_2 \quad = \quad CH_3\text{-}CO\text{-}O_2\text{-}NO_2 \text{ (PAN)} \qquad (1)$$

PAN can be formed in polluted air masses binding reactive nitrogen oxides (NO_2) and organic radicals. However, the reactive species can be released again from PAN by the backward reaction of equilibrium (1). This equilibrium strongly depends on temperature (cold temperatures favour PAN); if PAN is formed in the polluted planetary boundary layer and subsequently lifted into the cold upper troposphere it can by transported over large distances, leading to intercontinental transport of NO_x.

NO_y is continuously measured by Empa at the Jungfraujoch observatory (3580 m asl., JFJ) since 1999; measurements at Jungfraujoch allow studying polluted air advected from the European planetary boundary layer as well as air of the lower free troposphere including air transported of the Atlantic. PAN has been measured at Jungfraujoch in 1997-1998 (Zellweger et al., 2003) and in seasonal cmapaigns in 2005 by Balzani Lööv et al. (2008).

The goals of the project were: (a) continous field measurements at Jungfraujoch for PAN and additional NO_y measurements planned for a limited period in order to check the continuous measurements of Empa. Our NO_y instrument is very sensitive and it has been previously used in airplane campaigns and the inlet is mounted outside in order to minimize sampling errors (see Hegglin et al., 2006) allowing to check the possible effect of HNO_3 deposition inside the instrument operated by Empa; (b) the scientific analysis of the project is devoted to the composition of NO_y and its potenial changes making use of the additional measurements of PAN, NO_x (measured by Empa) and nitrate in particulates (kindly provided by PSI).

2. Field measurements performed at Jungfraujoch

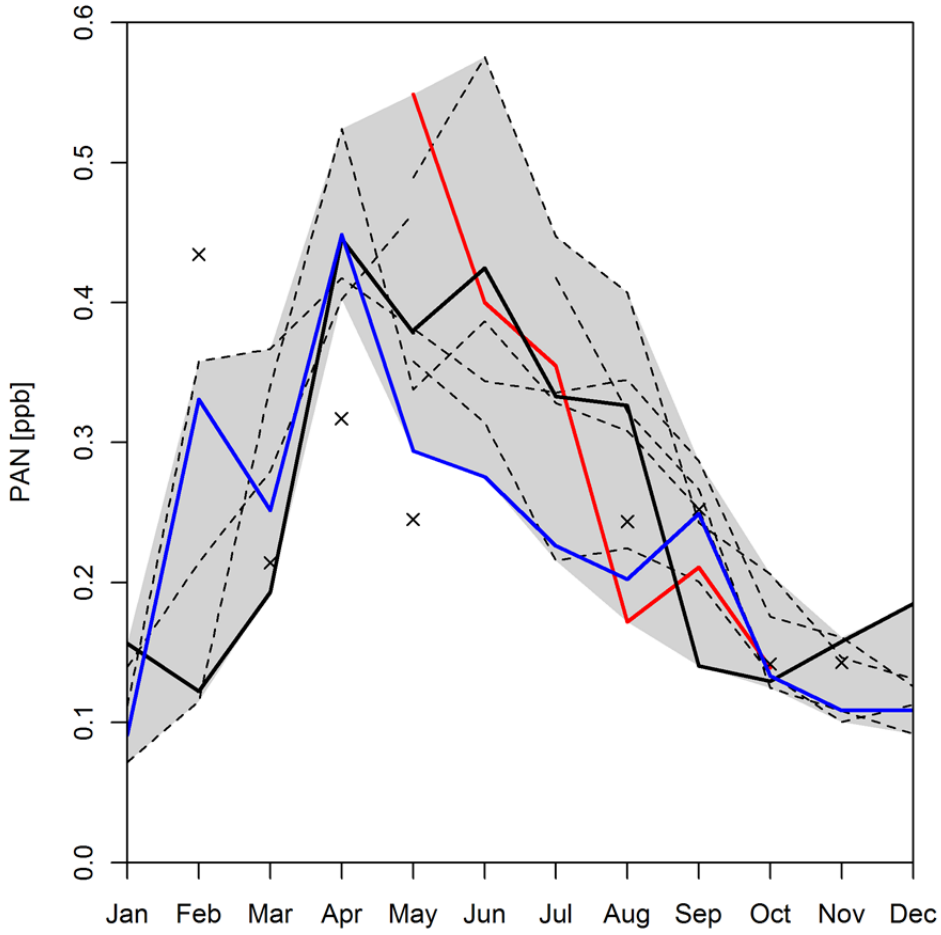

Figure 1: Mixing ratios of PAN measurements at Jungfraujoch: Monthly mean measurements of this study (2008 (red) and 2009 – 2010 (blue)) in comparison with the earlier data of Zellweger et al. (2003) (black solid line) and seasonal campaign measurements of Balzani Lööv et al. (2008) (black crosses) and measurements from the alpine site Zugspitze (2004 -2008, black dashed lines, and grey shaded area presenting the range of Zugspitze data).

Figure 1 presents an overview of PAN mixing ratios (monthly mean values) perfomed in our project in comparison with earlier measurements and from Zugspitze (Zugspitze is a high mountain site in southern Germany). The very senstivie instrument to measure NO_y, NO (and O_3) was successfully operated at Jungfraujoch from October 2009 to February 2010.

3. Analysis of field measurements

The seasonal variation of PAN at Jungfraujoch and the mountain site Zugspitze (southern Germany) typically shows highest monthly mean values in spring, usually in April or May (see Fig. 1). In order to study the seasonal variation of PAN we analyzed the very high PAN concentrations measured at Jungfraujoch and Zugspitze in May 2008 (see Figure 2) in detail. High pressure conditions in spring favor high PAN concentrations in the polluted PBL since solar UV-radiation is already high and temperature is still rather cold preventing thermal PAN decomposition. Backward trajectory analysis derived from the high resolution meterological forcast model COSMO showed that high PAN concentrations measured at Jungfraujoch and Zugspitze in spring 2008 were associated with transport from the polluted Planetary Boundary Layer air advected from eastern Europe or the polluted region from the Milan area (see Figure 3). The synoptic weather system during the period of high PAN concentrations in May 2008 was characterized by a high pressure system centered over northern Germany allowing for the required condition for high PAN formation in the planetary boundary layer and subsequent transport to the mountain sites.

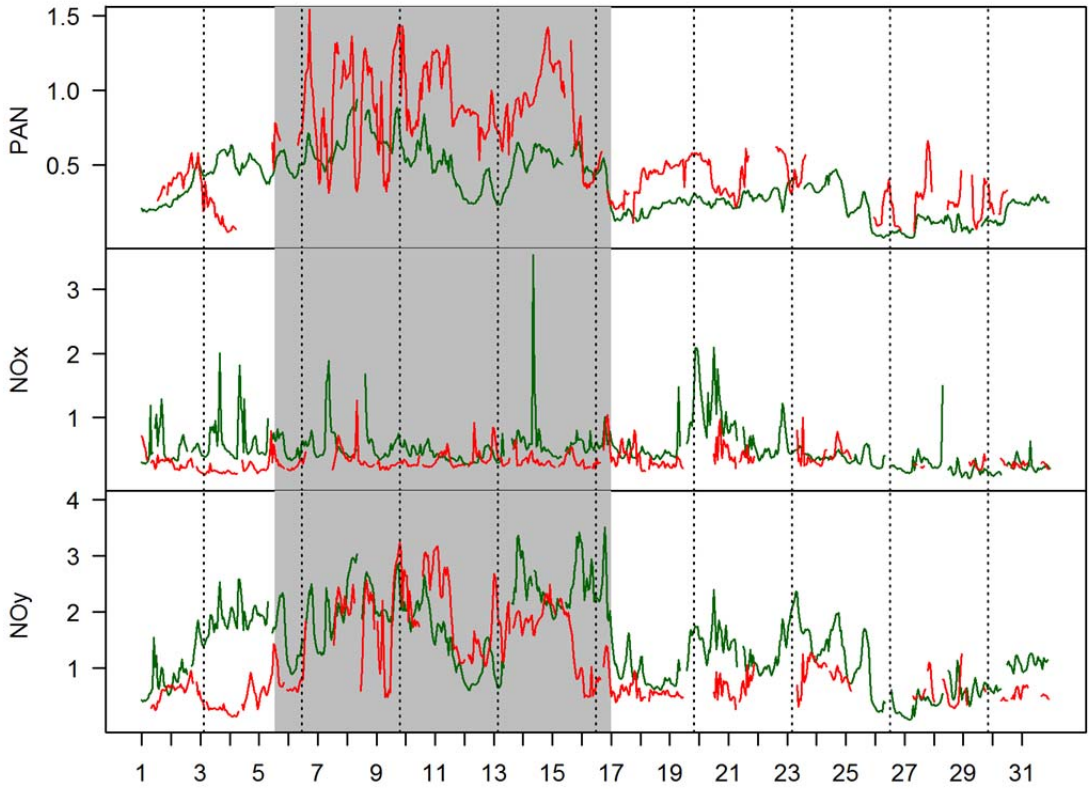

Figure 2: Trace gas measurements (PAN, NO_x and NO_y) at Jungfraujoch (red) and Zugspitze (green) in May 2008.

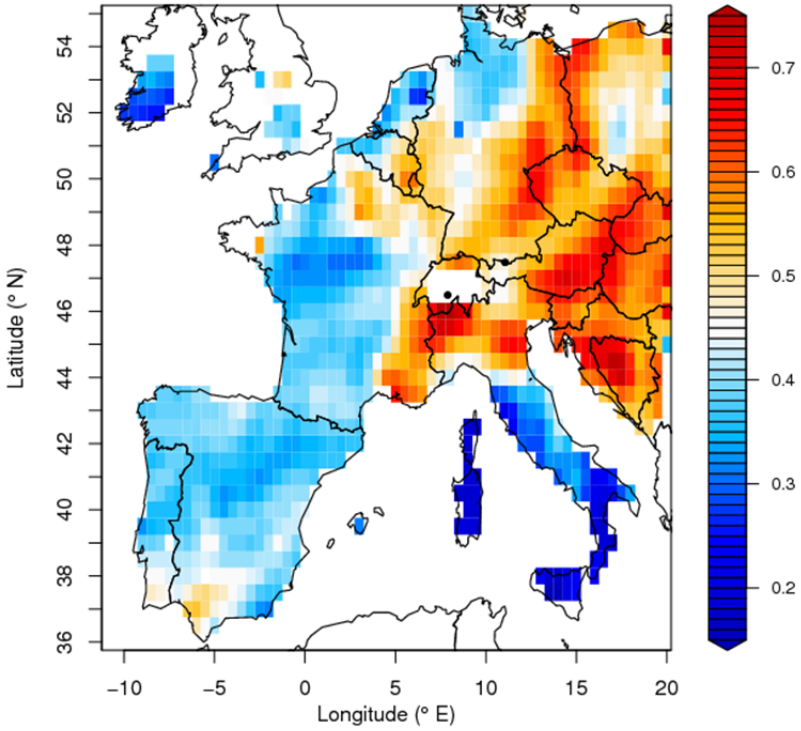

Figure 3: Transport path of the trajectories combined for Jungfraujoch and Zugspitze for May 2008.

4. Conclusions and outlook

PAN is a secondary air pollutant formed in tropospheric air in a similar way as O_3, namly by photooxidantion from its precursors (NO_x and VOCs). PAN measurements at Jungfraujoch were extended within this project showing record high mixing ratios in spring 2008. PAN mixing ratios also contain valuable information related to intercontinental transport of photooxidants which obtained large attention in recent years in the context of HTAP since increasing emissions in east Asia might affect air quality in North America and affect hemispheric ozone background. Numerical simulations were used to describe the effects of anthropognic emissions on the hemispheric distribution of photoxidants (e.g. Fiore et al., 2009). They indictaed that intercontinental transport in the northern hemisphere is most effective in spring. However, the results of this project indicate that the very high PAN mixing ratios measured at the European alpine sites measured in May 2008 are attributable to PAN formation in the polluted European boundary layer and not caused by intercontinental transport (see Section 3). PAN measurements of the European alpine sites will be used to explore the potential of PAN measurements from mountain sites in the context of the evaluation of numerical simulations used to describe intercontinental transport (Fiore et al. (2011).

Further analyses are under way to analyse the longterm NO_y series performed by Empa including the comparison with our NO_y campaign measurements (see Section 2) and the NO_y longterm evolution at Jungfraujoch and also in the context of changes in anthropogenic NO_x emission (see EEA, 2009). The comparison of the PAN measurements of this project with the earlier measurements of Zellweger et al., (2003) performed more than a decade is also planned. In this analysis the ratio of PAN and NO_x to NO_y (NO_y speciation) will be studied. NO_y speciation contains

valauable information about the oxidation history of an air parcel, because in tropospheric oxidation the primary NO_x species and PAN are gradually convereted into NO_y. However, variability in trace species at Jungfraujoch such as NO_y, PAN and NO_x is largely depending on emission, transport and chemical oxidation of the airmass. In order to describe the origin of the airmass and its transport pathway backward trajecories determined by the trajectory method Lagranto (as used by Cui et al., 2010) will be used.

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References

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Zellweger, C., J. Forrer, P. Hofer, S. Nyeki, B. Schwarzenbach, E. Weingartner, A. Ammann, and U. Baltensperger: Partitioning of reactive nitrogen (NO_y) and dependence on meteorological conditions in the lower free troposphere, *Atmos. Chem. Phys.*, 3, 779-796 (2003).

Planned publications from the project

Cui, J., S. Pandey Deolal, M. Sprenger, S. Henne, J. Staehelin, M. Steinbacher, and P. Nedelec: Free Tropospheric Ozone Changes Over Europe as Observed at Jungfraujoch (1990-2008): An Analysis Based on Backward Trajectories, *J. Geophys. Res.*, in revision.

Fiore, A., Jaffe, D., Fischer, E., Pandey Deolal, S, Dentener, F., and Staehelin, J., Hemispheric and regional, pollution signatures in PAN at northern mid-latitude mountain sites, in prep.

Pandey Deolal, S., S. Hennne, J. Staehelin, L. Ries, U. Weers, M. Steinbacher, T.Peter, E. Weingartner Seasonal variation of PAN at Jungfraujoch and Zugspitze: Analysis of spring 2008 data, in prep.

Key words:

Atmospheric trace gases, free troposphere, planetary boundary layer, tropospheric chemistry, NO_y, PAN

Internet data bases:

http://www.iac.ethz.ch

Collaborating partners/networks:

Martin Steinbacher, Stephan Henne, Christoph Zellweger, Dominik Brunner (Empa)

Scientific publications and public outreach 2010:

Refereed journal articles and their internet access

J. Cui, J., Pandey Deolal, S., Sprenger, S. Henne, S., Staehelin, J., Steinbacher, M., and Nedelec, P., Free Tropospheric Ozone Changes Over Europe as Observed at Jungfraujoch (1990-2008): An Analysis Based on Backward Trajectories, J. Geophys. Res., in revision.

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