Keynote: Oxidative capacity: from ground-based to airborne measurements

Horst Fischer, Max Planck Institute for Chemistry, Mainz (horst.fischer@mpic.de)

Most trace gases emitted into the atmosphere are oxidized to water soluble species by reactions with ozone and the hydroxyl radical. The rate of this self-cleansing process has been termed the oxidizing capacity of the atmosphere. Recently, field measurements of OH and HO_2 have become available. These measurements have been compared to state of the art photochemical models to test our understanding of atmospheric chemistry. Here we review HO_x chemistry in various environments from the marine boundary layer to the upper troposphere. Although good agreement is found in several environments, large differences between observations and models are found in particular in low NOx, high biogenic VOC environments.

Ozone is the second most important oxidant in the troposphere and it is the main precursor for OH. Thus a deep understanding on the photochemical ozone production in the troposphere is essential for its oxidizing capacity. A comparison of net ozone tendency rates deduced from in-situ observations with 3D-Chemical Transport Model simulations indicates a good understanding of the processes involved in ozone production and destruction. Nevertheless, investigations into the photo-stationary state of the $O_3/NO_x/RO_x$ system exhibit some deviations at low NO_x levels, potentially indicating the existence of a so far unidentified oxidizer.

Investigation of isoprene oxidation in the atmosphere simulation chamber SAPHIR at low NO concentrations.

Hendrik Fuchs, F. Rohrer, A. Hofzumahaus, B. Bohn, T. Brauers, H.-P. Dorn, R. Häseler, F. Holland, X. Li, K. Lu, S. Nehr, R. Tillmann, A. Wahner,

Institute of Energy and Climate Research, IEK-8: Troposphere, Forschungszentrum Jülich GmbH, Jülich, Germany (h.fuchs@fz-juelich.de)

During recent field campaigns, hydroxyl radical (OH) concentrations that were measured by laser-induced fluorescence spectroscopy (LIF) were up to a factor of ten larger than predicted by current chemical models for conditions of high OH reactivity and low nitrogen monoxide (NO) concentrations. These discrepancies were observed in the Pearl-River-Delta, China, which is an urban-influenced rural area, in rainforests, and forested areas in North America and Europe. Isoprene contributed significantly to the total OH reactivity in these field studies, so that potential explanations for the missing OH focused on new reaction pathways in the isoprene degradation mechanism. These pathways regenerate OH without oxidation of NO and thus without ozone production. In summer 2011, a series of experiments was carried out in the atmosphere simulation chamber SAPHIR in Juelich, Germany, in order to investigate the photochemical degradation of isoprene at low NO concentrations (NO<300pptv). Reference experiments with CO proved that measured radical concentrations could be accurately predicted in SAPHIR by established chemical models like the Master Chemical Mechanism (MCM). Moreover, OH concentration measurements of two independent instruments (LIF and DOAS) agreed during all chamber experiments. Here, we present the results of the experiments and compare measurements with model predictions using the MCM. Furthermore, the validity of newly proposed reaction pathways in the isoprene degradation is evaluated by comparison with observations.

Volatile organic compounds: measurements with the new Ultra-LightWeight PTR-MS

Felix Geiger[1], C.Warneke[2,3], M.Graus[2,3], J. de Gouw[2,3], J. M. Roberts[2], J. Gilman[2,3], B. Lerner[2,3], G. Petron[2,3], J. Kofler[2,3], F. Helleis[4], M. Neumaier[1] and A. Zahn[1]

[1] Institute for Meteorology and Climate Research, Karlsruhe Institute of Technology, Karlsruhe, Germany, (felix.geiger@kit.edu)
[2] Earth System Research Laboratory, National Oceanic and Atmospheric Administration, Boulder/CO, USA
[3] CIRES, University of Boulder, Boulder/CO, USA
[4] Electronics, Max Planck Institute for Chemistry, Mainz, Germany

Volatile organic compounds (VOCs) play a key role in atmospheric chemistry – inter alia regarding the oxidative capacity of the troposphere and lowermost stratosphere. Airborne in situ measurements of VOCs can be performed in real time and high resolution with Proton-Transfer-Reactions Mass Spectrometry (PTR-MS).

Especially for airborne applications size and weight are very crucial parameters. The newly built system ULW-PTR-MS (Ultra-LightWeight Proton-Transfer-Reactions Mass Spectrometer) is compact and particularly lightweight (~50 kg) by designing of custom-built electronics and a new vacuum system and therefore predestinated for the application on research aircrafts (like HALO).

ULW-PTR-MS was fielded the first time on ground during UBWOS 2012 (Uintah Basin Winter Ozone Study) – an air quality study regarding the wintertime ozone exceedances linked to the natural oil and gas production. Direct comparisons and measurements between ULW-PTR-MS and the well introduced systems NOAA-PTR-MS (de Gouw & Warneke 2007) and NOAA-GC-MS (Goldan 2004) have been performed at the field site Horsepool. The agreement between the three instruments was very good, which attests the new ultra-lightweight system high accuracy.

ULW-PTR-MS can be used to gain information about:

- precursors of OH (e.g. acetone, formaldehyde)
- precursors of O_3
- tracers for biomass burning (e.g. acetonitrile)
- tracers for biogenic emissions (e.g. isoprene, terpenes)
- the origin of air parcels

The combination of the regularly used PTR-MS instrument on board passenger aircraft (project CARIBIC, since 2006) and the highly focused operations of ULW-PTR-MS onboard the research aircraft HALO will lead to a better understanding of chemical and dynamical processes of organic trace gases and their following products in the atmosphere.

Multi-gas observations with DOAS at different locations world wide and combination with future airborne measurements

Denis Pöhler Institute of Environmental Physics, Heidelberg, Germany (denis.poehler@iup.uni-heidelberg.de)

DOAS measurements are widely used in the scientific community for the remote sensing of a large range of trace gases. The measurement techniques can be separated in two groups, active and passive using artificial and natural light sources like the sun respectively. The Long Path (LP-) DOAS averaging over long distances, the White DOAS and the Cavity Enhanced (CE-) DOAS are in-situ techniques and belong all to the active technique. Multi Axis (MAX-) DOAS, Satellite, and many more belong to the passive techniques. Active DOAS has the advantage to measure over a larger spectral range. Passive DOAS can for example with MAX-DOAS derive vertical profiles. Many measured trace gases are relevant for the oxidation capacity of the atmosphere beginning from NO2, O3 over e.g. HONO, HCHO, Glyoxal, VOCs to halogens.

Some measurements of the last years will be presented. They are performed in cities with high, e.g. Hong Kong and medium pollution, e.g. Heidelberg, sub urban areas up to remote areas at coasts and polar areas. Depending on the location different gases are relevant in terms of the oxidation capacity. Only few observations are combined with airborne measurements, which could in many situations enhance significantly the understanding of the atmospheric processes. For example they are useful to giving us a picture of the trace gas distribution, plume propagation chemical life time and slow reaction mechanisms. Heidelberg therefore constructed a 3D imaging DOAS system for the HALO airplane. First flights with this instrument on other aircrafts will be presented.

Assessment of the role of stabilized Criegee intermediates in OH radical measurement by LIF

Anna Novelli[1], K. Hens[1], D.Kubistin[1, 3], C..Tatum Ernest[1], K. Trawny[1], M. Rudolf[1], P.Paasonen[2], M. Sipilä[2], P. Keronen[2], T. T Petäjä[2], T. Elste[4], C. Plass-Dülmer[4], H. Fischer[1], J. Williams[1], L. Vereecken[1], M. Martinez[1], J. Lelieveld[1], H.Harder[1].

1. Airchemistry, Max Planck Institute chemistry, Mainz, Germany.
2. Physics, University of Helsinki, Helsinki, Finland.
3. School of Chemistry, Univeristy of Wollongong, Wollongong, NSW, Australia.
4. German Weather Service, Hohenpeissenberg, Germany.

(anna.novelli@mpic.de)

Sulfuric acid in the gas phase plays a central role in new particle formation and in particle growth. Fine particles directly affect human health via inhalation and have an important impact on climate. In the gas phase, sulfuric acid is known to be formed from the oxidation of SO_2 by the OH radical in the presence of oxygen and water. In the last decade, new measurements of OH and H_2SO_4 have shown relatively high concentrations of H_2SO_4 during nighttime when the corresponding concentration of OH radicals was too low to explain such high concentrations of sulfuric acid. New laboratory experiments, in addition to theoretical studies, have shown that a possible candidate for the oxidation of SO_2 is Stabilized Criegee Intermediates (SCIs) arising from the ozonolysis of alkenes. The rate coefficient for the reaction of $CH_2OO + SO_2$ has been measured at 3.9×10^{-11} cm^3 $molecule^{-1}$ s^{-1} indicating a probable competing role for the SCI in the production of sulfuric acid.

Measurements of a fraction of atmospheric SCIs with laser-induced fluorescence (LIF) have been made using a chemical subtraction method both in the laboratory and in the field. The SCIs undergo unimolecular decomposition at low pressure inside the instrument forming OH that is then detected. Model results and laboratory tests confirm our findings. This new instrumental setup has been used in several environments including Finland (HUMPPA-COPEC), Spain (DOMINO HOx) and Germany (HOPE 2012) revealing a unique SCI signal strongly influenced by different kinds of vegetation and meteorological conditions.

Results from the HUMPPA campaign show a missing H_2SO_4 production after taking into account the contribution of the OH radical. The SCIs signal measured with our instrument shows a good correlation with this missing production confirming the important role of the SCI in the oxidation of SO_2 and in the formation of sulfuric acid. Using the missing H_2SO_4 production rate together with the rate coefficient for the reaction $CH_2COO + SO_2$, it has been possible to calculate a lower limit for the concentration of SCIs in the atmosphere, while the estimated VOCs concentration from the total OH reactivity provides an upper limit.

OH and HO_2 Measurements in a Rural Mid-Latitude Environment during HOPE2012

Cheryl Tatum Ernest[1], A. Novelli[1], K. Hens[1], K. Trawny[1], M. Rudolf[1], T. Elste[2], A. Werner[2], J. Englert[2], S. Gilge[2], C. Plaß-Dülmer[2], J. Lelieveld[1], M. Martinez[1], H. Harder[1]

1 Max Planck Institute for Chemistry (MPIC) (cheryl.ernest@mpic.de)
2 German Weather Service (DWD), Meteorological Observatory Hohenpeißenberg

Measurements of OH are necessary to properly understand many atmospheric processes. Its short lifetime and low ambient concentration provide challenges to in-situ measurements. During the HOPE2012 campaign, simultaneous measurements were performed using chemical ionization mass spectrometry (CIMS; DWD) and laser-induced fluorescence (LIF; MPIC). Direct comparison between the two instruments shows good agreement and supports the usage of LIF as a robust detection method. HO_2 is closely linked to OH in the atmosphere and was measured using LIF following chemical conversion to OH after reaction with NO. RO_2 radicals also produce OH after reaction with NO and may cause interferences for HO_2 measurements. Lab tests suggest that the interference from the reaction of small alkanes with OH via H-atom abstraction is small, while that from the OH addition reactions of alkenes, including isoprene, and aromatics can be significant. We have developed a method to characterize and correct for these RO_2 interferences. HOPE2012 provided the first field measurements using the MPIC LIF instrument since the confirmation of the RO_2 interference in lab and model data. The HO_x data obtained using LIF have also been used together with supporting measurements performed during HOPE2012 to examine the preliminary HO_x budget.

Keynote: Recent and future exploration of tropospheric chemistry using the French airborne facilities

Agnès Borbon, Lab. Interuniversitaire des Systemes Atmosphériques (LISA) IPSL, UMR 7583 CNRS, University of Paris Est Créteil and Paris Diderot (Agnes.Borbon@lisa.univ-paris12.fr)

Over the past decade, French research aircraft have been involved in various field campaigns with a focus on a better understanding of tropospheric chemistry. Various environments have been explored from polluted source regions (i.e. ESCOMPTE around the Marseille region, ESQUIF and, more recently, MEGAPOLI around Paris megacity) to remote areas (i.e. West Africa during AMMA). I will present an overview of the questions that were addressed and the key findings. Future research will be discussed in particular regarding the ChArMEx initiative on the Western part of the Mediterranean Basin.

Nitrogen oxides and reactive nitrogen in the UTLS: Long term observations from CARIBIC

Helmut Ziereis, DLR-Institut für Physik der Atmosphäre, Oberpfaffenhofen (Helmut.Ziereis@dlr.de)

Nitrogen oxides and total reactive nitrogen have a decisive influence on the chemistry in the upper troposphere and lower stratosphere (UTLS). Nitrogen oxide act as catalyst in several reaction chains influencing the cycling of OH, the production of ozone and the destruction of methane.

The impact of additional emitted nitrogen oxides for example by aircraft depends on the background composition of the atmosphere. However, there is a high uncertainty of the abundance of nitrogen oxides in the UTLS. Most nitrogen oxides data in the UTLS have been obtained by focussed aircraft missions and might be biased.

During more than seven years a large set of NO and NO_y data has been obtained in the UTLS. These data have been acquired within the CARIBIC project (Civil Aircraft for the Regular Investigation of the Atmosphere Based on an Instrument Container) on a monthly base using a Lufthansa Airbus A340-600.

The present data set of reactive nitrogen is suitable to form the base for an observational climatology. The large scale seasonal and regional distribution of nitrogen oxides at the UTLS is presented and compared to other measurements and the results of model simulations.

Mass-spectrometric observations of VOCs: Comparison of HALO with global monitoring onboard passenger aircraft

Marco Neumaier[*], F.Geiger[*], R. Ruhnke[*], O. Kirner[‡] and A. Zahn[*]

KIT - Karlsruhe Institute of Technology, [*]Institute for Meteorology and Climate Research / [‡]Steinbuch Centre for Computing, Karlsruhe, Germany (marco.neumaier@kit.edu)

Since May 2005 the CARIBIC passenger aircraft (Civil Aircraft for the Regular Investigation of the atmosphere Based on an Instrument Container – Lufthansa, Airbus 340-600) measures ~100 trace gases and aerosol components in the UTLS (9-12 km altitude) on four long-distance flights per month. Acetone along with other VOCs like acetonitrile, methanol and acetaldehyde is measured with a PTRMS (proton-transfer-reaction mass spectrometer). As an example the impact of acetone photolysis to HO_x formation around the tropopause (TP) is compared to HOx production from ozone photolysis and subsequent reaction with water vapor (both likewise measured by CARIBIC). Our data analysis takes into account newer acetone photolysis rates (recommended by the JPL in Evaluation No. 17, JPL Publication 10-6) that question the former picture of acetone as being an important HO_x precursor in the dryer upper TP region. Modeling parameters not easily accessible via experiment like photolysis rates were taken from the ECHAM/MESSy Atmospheric Chemistry (*EMAC*) model. It can be shown that acetone photolysis contributes up to 40% to the total (= acetone and ozone photolysis) HO_x production rate at the TP in autumn and around 25% in summer. Circa 2 km above the TP the contribution from acetone photolysis becomes even smaller due to the quickly decreasing volume mixing ratio of acetone at higher altitudes (~15% in summer and 20% in autumn).

Within the framework of the new EU project IGAS starting in January 2013 the PTRMS will be modified for the detection of further species and for higher sensitivity. As an example formaldehyde, whose detection sensitivity is limited due to its rather small proton affinity, plays a substantial role in the oxidative capacity of the troposphere. The more global distributions observed during CARIBIC around the TP region will serve as a representative climatology of selected VOCs for comparison of observations during future HALO campaigns (OMO-EU, OMO, EMERGE, CAFE).

Measurements of Stable Carbon Isotope Ratios in Atmospheric VOC during airborne campaigns

Marc Krebsbach, E. Hösen, R. Koppmann, P. Knieling, C. Linke, M. vom Scheidt, H. Spahn, J. Wintel (m.krebsbach@uni-wuppertal.de)

University of Wuppertal, Atmospheric Physics Department, Wuppertal, Germany

The assessment of the impact of VOC on the atmosphere can be significantly improved by measurements of stable carbon isotope ratios in VOC. Since this is a relatively new technique, data coverage is rare and more or less restricted to ground-based measurements. Nevertheless, measurements of stable carbon isotope ratios are a sensitive tool to study the atmospheric processing of VOC, to investigate the VOC distribution and to infer transport pathways. In addition, the isotopic information can help to differentiate between impacts of mixing and chemical processes and to estimate the residence times of the compounds in the atmosphere.

During the field campaign ZEPTER-2 in autumn 2008, whole air samples were collected on the Zeppelin NT in the planetary boundary layer and the lower free troposphere over south-west Germany. The air samples were analysed for stable carbon isotope ratios in VOC with GC-C-IRMS (gas chromatograph combustion isotope ratio mass spectrometer) in the laboratory later on. For toluene, one of the major anthropogenic pollutants, a source isotope ratio of $\delta^{13}C = -28.2 \pm 0.5$ ‰ was derived. To differentiate between dilution processes and photochemical degradation the concept of the effective kinetic isotope effect was used. In addition, the photochemical age of various compounds were estimated.

In August 2010 the modified Zeppelin air sampling system was deployed on the CASA C-212-200 during the VERDRILLT campaign in Spain. On three flights above different land and vegetation formations whole air samples were collected up to a height of 1600 m above ground. The substances with the prominent volume mixing ratios were acetaldehyde (max. 15.7 ± 0.3) ppbV and methanol (max. 8.7 ± 0.3) ppbV. The mean photochemical age for toluene was estimated to 2.5 ± 0.5 days, which is within the range of the known mean atmospheric lifetime. The isotopic signatures of all identified VOC span a range of 50 ‰. $\delta^{13}C$ values of chloromethane, i-butane, methanol, ethanol, aceton, benzene, pentanal, toluene, n-hexanal und ethylbenzene coincide with previous data reported in the literature. $\delta^{13}C$ values of acetaldehyde, dichlorofluoromethane, n-pentane, MEK, m/p-xylene und β-pinene expand the current literature data. For the first time $\delta^{13}C$ values of carbon disulphide, 2,3-butanediol, n-butanal, methyl acetate and isopropanol could be derived. The automated high volume air sampling system MIRAH has been deployed during the HALO TECHNO mission in October 2010 and the TACTS (Transport and Composition in the UTLS) campaign in August and September 2012. In addition, MIRAH was deployed in a part of the ESMVal (Earth System Model Validation) missions. In total 212 samples were collected between 80°N – 65°S and 25°W–73°E

in a height region up to 15 km. We determined stable carbon isotope ratios of several aldehydes, ketones, alcohols, and aromatics. Preliminary results will be shown.

Keynote: Small aircraft and small teams for big science

Bruno Neininger, Metair AG: Meteorological airborne observations measurements and expertise, Switzerland (bruno.neininger@metair.ch)

Airborne atmospheric research and earth observation knows a variety of tools and methods, and is dealing with even more scientific questions. Generally speaking, it's bringing instrumentation up into the atmosphere, allowing measurements of high quality under the given conditions. When dealing with atmospheric chemistry, the instrumentation has to quantify several trace gases at low ambient concentration with a sufficient accuracy. For studies dealing with long-range transport, exchange between the stratosphere and the troposphere, and substances that need heavy laboratory equipment for their detection, large aircraft with long endurance and high maximum altitude are necessary. However, as the atmosphere has several scales, also the transport of trace gases from their sources, and their chemical reactions, are acting on different scales. For many studies on the mesoscale, smaller aircraft are sufficient, or have considerable advantages like lower cost or flexible availability. Nevertheless, the scientific equipment of small aircraft can be quite advanced. Examples of urban plume studies with METAIR-DIMO and partners will be shown, documenting concentration fields and transport of nitrogen oxides, NMHC's, CO, O_3, and CO_2. Later, the focus was on the exchange of CO_2, H_2O and CH_4 between the soil (including anthropogenic sources), and the atmosphere. Presently we see a trend towards even smaller systems on UAS (Unmanned Aerial Systems) or RPA (Remotely Piloted Aircraft). The aim of the presentation will be to remind the community that studies about similar questions as in TOXCA could partly be performed with smaller tools, supplementing the large infrastructures that are necessary for global atmospheric research. This should trigger a discussion about the chances for today's scientific community, and the role of the small operators also in terms of funding.

Atmospheric oxidation capacity over Borneo during the SHIVA aircraft campaign

Katja Großmann[1], M. Dorf[1], M. Kenntner[1], K. Pfeilsticker[1], V. Catoire[2], H. Schlager[3], D. Oram[4], G. Mills[4], F. Hendrick[5], I.Desmedt[5], Y. Huan[5])

[1]Institute of Environmental Physics, Heidelberg, Germany
[2]Centre National de la Recherche Scientifique (CNRS), Orléans, France
[3]German Aerospace Center (DLR), Oberpfaffenhofen, Germany
[4]School of Environmental Science, University of East Anglia, Norwich, UK
[5]Belgian Institute for Space Aeronomy (IASB-BIRA), Brussels, Belgium
(Katja.Grossmann@iup.uni-heidelberg.de

Airborne measurements were carried out during the SHIVA (Stratospheric ozone: Halogen Impacts in a Varying Atmosphere) campaign at Miri, Malaysia in November and December 2011. The dataset was collected during 16 sorties of the DLR (Germany's national research center for aeronautics and space) research aircraft “Falcon” over Borneo comprising different flight profiles, which covered the boundary layer up to 12 km altitude.

During the sorties the detection of frequently elevated levels of isoprene and other volatile organic compounds (VOCs) emitted mainly from the tropical forests in Borneo, $C_2H_2O_2$ formed as a by-product in the VOC oxidation, the intermediately formed CH_2O and CO as end-product of the oxidation chain, indicates an elevated photochemical oxidation potential, mostly driven by OH formed in the photolytic destruction of CH_2O. Local air pollution of NO_x was detected, possibly due to fossil fuel combustion, biomass burning, oil rigs, and ship emissions, and from local traffic sustaining favorable NO_x levels for OH being elevated. Moreover, signatures of CH_2O and CO were detected in the outflow of convective clouds, indicating rapid transport of polluted near surface air into the upper troposphere.

The presentation will report on these findings and draw conclusion on likely major photochemical processes in pristine marine and terrestrial air, polluted air, and air transported into the upper troposphere.

Peroxy radical measurements over Spain within the EUFAR project VERDRILLT

M.D. Andrés Hernández[1], M. Horstjann[1], D. Kartal[2], M. Krebsbach[3], C. Linke[3], M. Lichtenstern[4], J.Andrey[5], I. Uria[6], T. Vera[7], and J.P.Burrows[1]

(1) Institute of Environmental Physics, University of Bremen, Germany
(2) presently at k3works GmbH, Treuchlingen, Germany
(3) Atmospheric Physics Department, University of Wuppertal, Germany
(4) DLR-Institut für Physik der Atmosphäre, Oberpfaffenhofen, Germany
(5) INTA, Madrid. Spain
(6) Univ. Pais Vasco, UPV-EHU, Spain
(7) CEAM, Centro de Estudios Ambientales del Mediterráneo Valencia, Spain

(lola@iup.physik.uni-bremen.de)

Peroxy radicals (HO_2 and RO_2, R being an organic chain) play a key role in the ozone production in the troposphere, the formation of peroxides and other oxidants. Investigating the vertical distribution of peroxy radicals in relation to the vegetation cover can provide valuable information about the extension of convective processes, and the relevance of surface emissions in the history and photochemical activity of air masses transported within the first few kilometers in the atmosphere.

The EUFAR project VERDRILLT **(VER**tical **D**istribution of **R**adicals **I**n the **L**ower **L**ayers of the **T**roposphere) leaded by the IUP-Bremen in cooperation with the DLR (Deutsches Zentrum für Luft- und Raumfahrt), the University of Wuppertal, the CEAM (Centro de Estudios Ambientales del Mediterráneo) and the UPV-EHU University in Bilbao aimed at getting a deeper understanding of the vertical distribution of peroxy radicals in the lower layers of the troposphere. Measurements of peroxy radicals and a suite of related trace gases were carried out on board of the INTA (Instituto Nacional de Técnicas Aeroespaciales) C212 aircraft over Spain in summer 2010. The flight tracks started and ended in Madrid leading to the Mediterranean and to the Cantabrian coasts respectively in an attempt to follow some pathways for the horizontal transport of pollutants from the coast to the interior of the Iberian Peninsula. The vertical distribution of trace gases measured in selected rural and urban areas under conditions favouring active photochemistry and convection are presented and discussed.

HOx radical measurements in the planetary boundary layer: Deployment of the airship Zeppelin NT

Frank Holland, M. Bachner, S. Broch, H. Fuchs, S. Gomm, A. Hofzumahaus, K. Kubik, A. Oebel, D. Raak, B. Bohn, A. Kiendler-Scharr, T. Mentel, F. Rohrer, A. Wahner

Institute of Energy and Climate Research, IEK-8: Troposphere, Forschungszentrum Jülich GmbH, Jülich, Germany (f.holland@fz-juelich.de)

The investigation of the distribution of trace gases in the lowest part of our atmosphere, the planetary boundary layer (PBL), has been proven a difficult task since the access to this shallow layer of air with (a) a complex suite of instruments including radical measurements and (b) flight characteristics which allow for slow motion and coverage of vertical profiles descending to heights close to ground was not possible due to missing airborne platforms. Since 2007 Jülich scientists make use of the airship ZEPPELIN NT which has unique properties: it can slowly hover and even stop in an air mass, can make vertical ascents and descents, and can fly up to 6h with a heavy instrumentation payload of 1000 kg. For the first time it is now possible to investigate the vertical distribution of trace gases, aerosols, and radicals in detail in the PBL (from 70 m to 1000 m above ground) which is the chemically most active region of our atmosphere. Results from the ZEPTER and PEGASOS campaigns with a focus on HO_x measurements will be presented.

Keynote: Lagrangian aircraft experiments for the investigation of photochemical transformation in polluted air masses

Hans Schlager, DLR-Institut für Physik der Atmosphäre, Oberpfaffenhofen (Hans.Schlager@dlr.de)

Lagrangian experiments are a powerful tool to study the photochemistry in pollution plumes during transport. The Quasi-Lagrangian approach is to measure the change of the composition of a single air mass as it moves by successive sampling flights. The Lagrangian connection between samples of the initial and aged plume provides insights into photochemical processes occurring on time scales of the experiment. The ability to quantify the chemical transformations during transport can be greatly enhanced by tagging the initial air mass with an artificial tracer for non-ambiguous air mass identification and information on mixing processes. Result from recent Quasi-Lagrangian aircraft studies will be presented and the technique of tagging and tracking air-masses will be discussed. The capabilities for future Lagrangian experiments using the HALO aircraft will also be addressed.

Application of an imaging DOAS instrument for tropospheric trace gas mapping

Anja Schönhardt, Institute of Environmental Physics, University of Bremen, Germany (schoenhardt@iup.physik.uni-bremen.de)

The recently developed and tested imaging DOAS instrument provides the opportunity of trace gas measurements in the troposphere with good spatial resolution. In the current setup, the instrument is viewing in nadir geometry and is adjusted for measurements of NO_2. It may be changed and optimized in the future for alternative trace gases, such as Glyoxal, Formaldehyde, BrO, SO_2 and others.

The imaging DOAS instrument provides good measurement sensitivity and fine spatial resolution on the order of 100 m and is therefore suitable for dedicated pollution measurements. Measurement results are in addition useful as model input, for comparisons with model calculations, for satellite validation and for information on sub-pixel variability.

During first flights on the Polar-5 aircraft the instrument performance, imaging quality, and ability for NO_2 detection have successfully been investigated. One research flight was conducted above a black coal power plant, where mapping of the NO_2 exhaust plume has been performed and emission fluxes may be determined.

The influence of different pollution sources on the chemical composition of the Arctic troposphere: Observations during the ACCESS project

Anke Roiger, DLR-Institut für Physik der Atmosphäre, Oberpfaffenhofen (Anke-Elisabeth.Roiger@dlr.de)

Impacts of global warming lead to an increase of pollution import into the polar region, as well as to an enhancement of local emissions in the Arctic. Since the 1960s, the Arctic Ocean ice cover has decreased by 50%. Transpolar shipping and hydrocarbon resource extraction therefore is expected to heavily increase in the foreseeable future. Transport of pollution into the polar region already is enhanced, mainly due to import of Siberian and North American biomass burning emissions. Within the framework of the ACCESS project (Arctic Climate Change, Economy and Society), we performed aircraft-borne measurements in the Arctic in July 2012 in order to study the influence of different pollution sources on the chemical and aerosol composition of the Arctic. The DLR Falcon was based in Andoya, northern Norway, and conducted 13 research flights studying Arctic pollution. Thereby emissions and distributions of trace compounds were measured including nitrogen oxides, hydrocarbons, sulfuric dioxide, and particulate matter, e.g. black carbon. During low-level flights, emissions of different vessel types (passenger-, cargo and fishery ships) and of oil platforms located in the Norwegian Sea were sampled. These measurements will be used to study primary emitted pollutants and formation of secondary trace gases and particles in the exhaust gas. During large-scale flights above the Barents Sea, pollution originating from Russian industrial areas located in the Arctic, as well as from Siberian biomass burning source regions was probed. The Falcon measurements will be used to improve emission inventories and to validate model simulations. This will help to improve model predictions of future Arctic pollution and warming.

European Space Agency Campaign Activities in Support of Earth Observation Projects

Dirk Schüttemeyer, M. Davidson, P.l Ingmann, J. Langen, Y. Meijer, A.-G. Straume, B. Veihelmann, T. Wehr

European Space Agency, Keplerlaan 1, 2200 AG Noordwijk ZH, The Netherlands
(dirk.schuettemeyer@esa.int)

In the framework of its Earth Observation Programmes the European Space Agency (ESA) has been conducting airborne and ground-based measurement campaigns since 1981 to support geophysical algorithm development, calibration/validation, simulation of future spaceborne earth observation missions, and applications development related to land, oceans and atmosphere.
Campaign activities include experiments related to atmospheric dynamics, atmospheric chemistry, coasts and oceans, ice and land surfaces by deploying a broad range of active and passive instrumentation in both the optical and microwave regions of the electromagnetic spectrum.

The Agency usually does not conduct experiments in isolation but seeks collaboration with national research organizations in the ESA member states as well as with international organizations. There are two main reasons for this. Firstly it has always been a strategic objective to harmonize European campaign activities and to favour cooperation between international organizations and national research programs. Secondly, the financial frame of ESA's campaign activities has fostered collaboration, taking advantage of projects initiated and funded by external partners. For the different activities a rich variety of datasets has been recorded, are archived and users can access campaign data through the EOPI web portal [http://eopi.esa.int].

The main objective of this paper is to highlight the general setup for campaign execution and give examples of on-going and planned activities in the context of atmosphere related candidate or approved future missions, like Sentinel 4/5/5p, Premier, CarbonSat, ADM Aeolus and EarthCARE.

Examples for on-going campaign activities will include the identification and quantification of greenhouse gases (CO_2, CH_4), NO_2 and aerosols. Examples for planned activities will focus on the latest developments in the context of upcoming calibration/ validation preparations.

Keynote: Exploiting atmospheric field measurements with numerical models.

Mattew Evans, National Centre for Atmospheric Science, Department of Chemistry, University of York (mat.evans@york.ac.uk)

Atmospheric chemistry is a young science and is still primarily ‘observationally driven. The usefulness of these observations is increased many-fold through the use of numerical models. These models play a central role in assessing the consistency of our understanding, filling in observational gaps, forecasting the future atmospheric state and providing input into policy. These models take many forms, from simple local steady state approximations, through box models, and onto transport, climate and Earth system models.

In this talk I’ll give some examples of observation - modelling studies that have been successful in driving science forwards and discuss the numerical and experimental techniques that proved successful. I will also discuss some of the difficulties associated with using observations and models in a coherent way. I will conclude with a discussion of where I feel the future lies in exploiting observations of atmospheric composition with numerical models.

What can we expect to measure? – Simulated aircraft measurements of NO_2 in the BeNeLux and Po Valley using BOLCHEM simulations.

Andreas Hilboll[1] and Alberto Maurizi[2]

[1]Institut für Umweltphysik, Universität Bremen (hilboll@uni-bremen.de)
[2]CNR ISAC Turbulence and Dispersion, Bologna, Italy

Measurements of tropospheric NO_2 are an invaluable tool to estimate anthropogenic NOx emissions and their influence on the oxidizing capacity of the atmosphere. Aircraft-based measurements can be especially helpful in this respect as they allow to measure NO_2 concentrations at varying geolocations and altitudes within a short time. This enables flux estimations for encircled areas, like e.g. megacities or pollution hot-spots.

By using a high-resolution (10km) of the BOLCHEM chemistry and transport model with hourly output, I'll show an easy way to simulate aircraft measurements of tropospheric NO_2 concentrations. This allows to analyze possible results already during the planning phase of an aircraft measurement campaign, and to adjust the flight path to the expected spatial-temporal NO_2 patterns. Additionally, the modelled NO_2 fields allow to estimate the representativeness of the measured NO_2 concentrations at an individual time, as the temporal variability of the tropospheric fields can be very large.

Keynote: Fields campaign analysis with the EMAC global model

A.Pozzer[1], D. Taraborrelli[1], P. Joeckel[2]

[1] Atmospheric Chemistry Department, Max-Planck Institute for Chemistry, Mainz.
[2] Deutsches Zentrum fuer Luft- und Raumfahrt, IPA, Oberpfaffenhofen, Germany
(andrea.pozzer@mpic.de)

Atmospheric chemistry models heavily rely on observations for their evaluation and further development. In particular, observations from field campaigns are essential for a specific evaluation of the model behavior. A well designed field campaign can drive the improvement of process representation inside global models. However, most of the time global models do not resolve the spatio-temporal scales of important processes that influence the observations.

Here we discuss the standard approaches that are adopted to compare model results and observations. Few practical examples using the EMAC (ECHAM5-MESSy for Atmospheric Chemistry) will be given, focusing on organic compounds distribution and the atmospheric oxidation capacity. From the global modeling perspective, we discuss the ideal spatio-temporal coverage of a field campaign. Finally we mention observations which would help us to shed light on processes like HO_x cycling and organic acid production.