A21A MCC: 3016 Tuesday 0800h

Biogenic Reactive Trace Compounds and Their Role in Atmospheric Chemistry and Climate I *(joint with B, OS)*

Presiding: **A H Goldstein,** University of California**; A Hansel,** University of Innsbruck

A21A-01 0800h INVITED

Seasonality affects the Emission of Biogenic Volatile Organic Compounds (VOC): Results from Studies within LBA and ECHO

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Seasonality exhibits large amplitudes in temperate forests. This is easily observed and well described for plant anatomical/morphological, cytological, and physiological attributes. Also the emissions of volatile organic compounds may exhibit a clear seasonality from low or zero emissions in winter to high emissions in summer. In contrast seasonality of tropical vegetation is classified as relatively indistinct. However, tropical climate does not mean constant environmental conditions, but also shows seasonality, i.e. dry and wet or flooding seasons. Short term environmental (climatic) effects may intensify seasonal fluctuations of VOC emissions triggered by temperature, light, water availability, developmental status and plant diseases. Recent results obtained in the course of LBA-EUSTACH (EUropean Studies on Trace gases and Atmospheric CHemistry as a contribution to the Large-scale Biosphere-Atmosphere experiment in Amazonia) and ECHO (Emission and Chemical Transformation of Biogenic Volatile Organic Compounds) are discussed.

A21A-02 0815h

Emission and Chemical Transformation of Biogenic Volatile Organic Compounds(ECHO)- Investigation in and above a Mixed Forest Stand: An Overview

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The objective of the ECHO project is to provide a better understanding of forest stands as a complex source of reactive trace gases into the troposphere. This will be achieved by a unique combination of field, laboratory, and simulation experiments investigating chemical and dynamical processes within the canopy and thus the forest stand as a net source of reactive trace compounds into the planetary boundary layer. The field experiments were carried out in the Stetternicher Forest on the area of the Research Center Jülich. The area has been a deciduous forest for more than 300 years and is surrounded by farmland. Dominating tree species are oaks, beech, and birch. Prevailing wind direction is from the south west, more seldom from the south east. The site is only weakly influenced by urban air masses. At the site three towers were set up, which were equipped with a large set of instruments to measure micrometeorological parameters, biogenic and anthropogenic volatile organic compounds, ozone, nitrogen oxides, and CO, as well as radiation in and above the forest. Additionally, measurements of meteorological parameters were done at the meteorological tower up to a height of 120 m and with a SODAR-RASS system up to 300 m. The first field study took place between June 3 and July 12, 2002, the second field campaign between June 23 and August 1, 2003. As a speciality of the ECHO project, important aspects of the different processes determining the net emission from forest stands into the atmosphere are investigated in laboratory and simulation experiments. The chemical processing of the trace gas mixtures observed in the forest stand is investigated in the atmosphere simulation chamber SAPHIR under controlled conditions. This enables a detailed study of the chemical processes under exclusion of transport processes and sensitivity studies by direct modification of individual chemical parameters. Emission and uptake of VOC by plants are investigated in plant chambers under defined conditions. The soil as a source of nitrogen oxide is investigated in a lysimeter experiment. The flow dynamics of the forest site is investigated in detail in wind tunnel experiments using a 1:300 scale model of the field site.

URL: http://www.fz-juelich.de/icg/icg-ii/echo

A21A-03 0830h

Photochemistry in a Mixed Deciduous Forest: First Results of the Measurements of Isoprene and its Oxidation Products During two Years of the ECHO Project

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Isoprene contributes significantly to the regional tropospheric ozone formation. Forest stands are the largest sources of isoprene in the troposphere. During the last years various field studies have been carried out to measure isoprene and its oxidation products at rural sites. However, the interaction between photochemistry within the forest canopy and exchange processes with the PBL are not yet fully understood. One aim of the ECHO project (Emission and chemical transformation of biogenic volatile organic compounds) is to investigate to what extent the photochemistry within the canopy influences the net emission of isoprene and secondary products from the forest stand into the PBL. Here we present measurements of the mixing ratios of isoprene and its oxidation products methacrolein (MACR) and methy vinyl ketone (MVK) obtained in a mixed deciduous forest during the vegetation periods in 2002 and 2003. The measurements were carried out at a tower between 2 m and 36 m at different heights above ground. On the same tower comprehensive measurements of other trace gases (nitrogen oxides, ozone, free radicals, CO, PAN, HONO, and anthropogenic VOC), as well as photolysis frequencies and meteorological parameters were conducted in order to get insight into the influence of ambient trace gas levels and transport processes on the oxidation of isoprene and its oxidation products. During daytime mixing ratios of isoprene varied between 400 ppt at low ambient temperature levels and 5.8 ppb on hot and sunny days. During the night isoprene mixing ratios dropped to typical values of about 30 ppt. In June and July 2002 the ratio of MVK/MACR often was less than 1 which is in contrast to the product yield ratio found in other field and laboratory experiments. In 2003 the ratio changed from values of less than 1 in June to values up to 1.8 in August. This observation indicates that the oxidation of isoprene may be influenced by factors previously not considered. Based on these observations simulation experiments were carried out in the atmosphere simulation chamber SAPHIR (see contribution by M. Karl et al.). Together with the extensive measurements of mixing ratios of other trace gases, free radicals, photolysis frequencies, and meteorological parameters, the combination of field and simulation experiments allows to investigate the isoprene oxidation within a forest canopy at different ambient conditions.

URL: http://www.fz-juelich.de/icg/icg-ii/echo

A21A-04 0845h

Effects of high ambient temperature on plant physiology and the emission of monoterpenes, isoprene, and volatile organic carbon by beech observed during ECHO-field campaigns in 2002 and 2003

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The emission of volatile organic compounds (VOC) from 40-80 year old beech trees (Fagus sylvatica) was studied during two intensive field campaigns in the summers of 2002 and 2003 within the framewok of the ECHO (Emission and CHemical Transformation of volatile biogenic Organic compounds) project. Determination of VOC emission rates was performed by various conventional techniques (GC-FID, GC-MS, HPLC), but also by online analysis of total volatile organic carbon. High ambient temperatures (30-40^{o}C), as observed during both campaigns, were found to have a significant impact on plant physiology (assimilation, transpiration, and stomatal conductance), indicating a reversible stress condition, expressed in a diurnal reduction of CO2 uptake and water loss (midday depression). In parallel with this effect, the emission of volatile organics increased by two orders of magnitude, but also showed a hysteresis effect that followed the drop in net assimilation in the afternoon.

A21A-05 0900h

Uptake of Nitrogen Dioxide by Quercus robur - is There a Compensation Point?

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Within the German Atmospheric-Research-Program 2000, the project ECHO (Emission and CHemical Transformation of Biogenic Volatile Organic Compounds) has been carried out in a mixed forest stand during the summer of 2002. The contribution of the Max Planck Institute for Chemistry was the complete characterization of the NOx-flux within the forest, including (a) the quantification of the biogenic NO-release from forest soils, (b) the measurement of the vertical distribution of NOx within and above the canopy and (c) the turbulent transport within and above the forest. The profile measurements allow to identify the participating processes: soil NO emission and subsequent titration of emitted NO by ozone, advection of highly polluted air masses to the site and the uptake of nitrogen dioxide within the crown area. The latter, i.e. the role of vegetation in the NOx-budget within a particular ecosystem is still a matter in controversy, which translates into considerable uncertainties in the global NOx-budget. To assess this issue, dynamic cuvette measurements were performed on a Quercus robur branch. The concurrent measurement of plant physiological (leaf temperature, stomatal conductance,

transpiration and photosynthesis/respiration) and ambient parameters (radiation, ambient NOx mixing ratios) allows to put the exchange rate into context. The question whether a compensation point may be identified will especially be addressed.

A21A-06 0915h

Fluxes of Primary and Secondary Biogenic Volatile Organic Compounds (BVOC) During the BEWA Field Experiments

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Biogenic volatile organic compounds (BVOCs) play a crucial role in the formation of photo-oxidants and particles through the diverse BVOC degradation pathways. Yet, current estimations about temporal and spatial BVOC emissions, including the specific BVOC mix are rather vague. This paper reports results from the determination of BVOC net emission rates that were obtained within the frame of the BEWA field experiments at the Waldstein site in the Fichtelgebirge in 2001 and 2002, an extended forest site that is largely dominated by Norway spruce (Picea abies [L.] Karst.). Stand fluxes of volatile organic compounds were determined with Proton Transfer Reaction Mass Spectrometry (PTR-MS) coupled to a Relaxed-Eddy-Accumulation (REA) system. The PTR-MS is capable to measure simultaneously a variety of organic trace gases, including oxygenated compounds. Air samples were taken at the top of a meteorological tower at the height of 32 m a.g.l. close to the Gill Sonic anemometer that controlled the REA-sampling. A critical value when using the REA approach is the Businger-Oncley parameter b. For this canopy type a b value of 0.39 (threshold velocity wo = 0.6) was determined. The PTR-MS data show clear diurnal variations of ambient air mixing ratios of isoprene and monoterpenes, but also of oxygenated VOC such as methanol, carbonyls, methylvinylketone (MVK) and methacrolein (MAC). Canopy fluxes of isoprene reached up to 7 nmol m^{-2} s^{-1} during daytime. The fluxes of the sum of monoterpenes were in the same range. MVK and MAC are products from isoprene oxidation. The BEWA data confirm this relationship and reveal a better correlation of MVK+MAC with isoprene (r^2=0.78) than with the sum of monoterpenes (r^2=0.30). In our study MVK+MAC fluxes were about 30% lower than isoprene fluxes. Both observations indicate active photochemical degradation of isoprene in this area. Actealdehyde and acetone are typical intermediate compounds in the photochemical degradation of both anthropogenic and biogenic VOCs. However, they may also be emitted directly. Growing evidence shows that beside anthropogenic significant biogenic sources exist for both compounds. The results of the BEWA campaign reveal only a poor correlation between acetaldehyde and acetone (r^2=0.02) indicating different origins of both species. The observations show that acetone deposition prevails suggesting that biogenic sources of acetone play a minor role, at least at this site. Acetaldehyde fluxes usually better agree with isoprene fluxes (r^2=0.55). However, they correlate best with MVK+MAC fluxes (r^2=0.81). This is an indication that acetaldehyde is primarily produced in photochemical degradation processes of VOC. Methanol canopy fluxes reached 22 nmol m^{-2} s^{-1} and daytime methanol mixing ratios were up to 15 ppbv and were comparable with previously reported values. The methanol mixing ratios are consistent with its relatively long atmospheric life time of approximately 16 days making advection an important issue. However, twig enclosure measurements during the summer 2002 intensive field experiment at the Waldstein site did not reveal significant direct methanol emissions.

A21A-07 0930h

Turbulent Exchange of Particulate Matter During BEWA2000

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During BEWA2000, two field campaigns were conducted in the "Fichtelgebirge" mountains, NE-Bavaria, Germany, to study biogenic emissions of volatile organic compounds from a "Norway Spruce" forest. BVOC oxidation products may contribute to particulate mass through condensation on existing particles or new particle formation. Measurements of particulate mass, particle size distributions and vertical particle fluxes were jointly analyzed and interpreted. The particle number flux system included a sonic anemometer and two condensation particle counters. Particle size distributions were measured with a differential mobility particle sizer at the same height as the flux system at 22 m agl. Also, particle number concentrations were measured within the forest stand. Particle mass was obtained from impactor and high-volume sampler measurements. Particle numbers differed considerably within and above the forest. The in-canopy concentration ranged from 60 % to 100 % of the concentration above the canopy. A diurnal pattern with effective particle production in the canopy through turbulent mixing and/or particle formation in the morning and effective particle removal in the canopy through deposition and/or coagulation processes in the afternoon was found. An important conclusion from these findings is that not only particle concentrations but also particle size distributions may differ within and above the forest. Turbulent particle number fluxes exhibited a diurnal pattern with small fluxes in the night and large fluxes during daytime. In general, particle deposition dominated over emission. A characteristic "banana-shaped" development of the particle size distribution indicating formation of particulate matter and subsequent growth was found on several days. Strong deposition fluxes occurred during these events. Particle mass fluxes may be determined from a combination of size distribution measurements and size-resolved deposition models. The mass determined from size distributions agrees well with directly measured particle mass. However, the uncertainty of calculated mass fluxes remains large. Funding by the German federal research ministry through grants PT BEO 51-0339476C and PT UKF 07ATF25 is gratefully acknowledged.

A21A-08 0945h

BEWA2000 Studies on the Regulation of Isoprenoid Biosynthesis as Prerequisite for the Development of Process-Based Emission Models

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Trees produce a wide spectrum of volatile organic compounds (VOCs) including isoprene and monoterpenes, as well as oxygenated compounds like aldehydes, alcohols and carboxylic acids. Aim of the BEWA2000 project within the German joint research project AFO200 (Atmosphaeren Forschungsprogramm 2000) is to elucidate the metabolic pathways leading to the formation of these compounds, in particular volatile isoprenoids. The presentation summarises information on photosynthetic and non-photosynthetic prercursors of isoprenoid biosynthesis, as well as on metabolites and enzymes of the plastidic isoprenoid pathway in isoprene- or monoterpene-emitting poplar (Populus spec.) and Holm oak (Quercus ilex). In particular, it discusses physiological, biochemical and molecular biological aspects, which are prerequisites for the development of process-based emission models describing the biochemical and physiological reactions leading to the emission of volatile isoprenoids.

URL: http://www.imk-ifu.fzk.de/bewa2000/

A21B MCC: 3018 Tuesday 0800h

Asian Outflow to the North Pacific and U.S. Western Coast *(joint with B)*

Presiding: **B J Huebert,** University of Hawaii**; D Parrish,** NOAA Aeronomy Laboratory

A21B-01 0800h

Meteorological mechanisms favoring Trans-Pacific Transport of Eurasian Pollutants on intraseasonal to interannual timescales

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We use a 10-year global 3-D model simulation to conduct a systematic analysis of the meteorological mechanisms leading to long-range transport of Eurasian pollutants to the Northeast Pacific atmosphere. We find that export of Asian and European pollutants in the lower troposphere over East Asia is strongly correlated with anomalously low sea level pressures over East Asia, especially during spring. This correlation reflects the dominant role of mid-latitude cyclones as an export mechanism for Asian pollutants. Import of Asian and European pollution to the Northeast Pacific below 3 km altitude is positively correlated with the intensity of the Pacific High with maximum correlation found in spring/winter. This highlights that advection around the Pacific High is an efficient pathway to transport pollutants across the Pacific over to the NE Pacific. Based on the centers of action found in the correlation analysis, we form teleconnection indices using sea level pressure (without the annual cycle) within two regions in the western and eastern Pacific. We compare these indices to intraseasonal and interannual variability in long-range transport and investigate their predictive ability in forecasting lower tropospheric trans-Pacific transport events. A similar analysis will be applied to long-range transport in the middle and upper troposphere.

A21B-02 0815h

Meteorological impact on eastern Asia tropospheric ozone during 1995-1996

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The impact of meteorology on eastern Asia tropospheric ozone distribution and transportation during 1995-1996 is researched by a regional scale chemistry model, which initial and boundary condition of species (O3, CO, and some long life VOCs) are obtained from a global chemistry model output. The comparison of model results with observations shows that the model reproduces the main diurnal and seasonal observed features. The differences of ozone distribution and transportation between years are mainly controlled by meteorology and meteorological factors combined with atmospheric chemistry processes, e.g., atmospheric cycle, cloud, precipitation and temperature. And the most obvious difference is found in April during 1995-1996.