A31G-08 1205h

Planned Improvements for the WB-57F Aircraft

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NASA WB-57F aircraft have supported the atmospheric science community for over 30 years. Recent attention has focused on the chemistry and dynamics of the UTLS region of the atmosphere and several NASA sponsored field campaigns (ACCENT, CRYSTAL-FACE) have made critical use of the WB-57F's unique ability to carry large (3 ton) payloads during extended cruise at all altitudes from the lower troposphere to the lower stratosphere (20 km ceiling). In addition, the WB-57F's robust structure permits a large number and variety of instruments to be carried at inlet-favorable locations on the aircraft. In order to further improve the WB-57F's performance and unique utility to the atmospheric research and spacecraft validation communities, NASA is planning several upgrades to the WB-57F including state-of-the-art avionics and autopilot, landing gear replacement, maximum gross weight increase, engine replacement, and ultrapod installation. We will review the present WB-57F performance, plans for upcoming science campaigns, and plans for increased WB-57F payload, range, endurance, and ceiling resulting from the upgrades.

URL: http://jsc-aircraft-ops.jsc.nasa.gov/wb57

A31H MCC: 3001-3003 Wednesday 1145h

Carbon Cycle Modeling

A31H-01 1145h

Inverse Estimates of Anthropogenic Carbon Dioxide From Ocean Interior Carbon Measurements and Ocean General Circulation Models

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The ocean is an important sink for atmospheric carbon dioxide, and the exchange of carbon dioxide between the atmosphere and ocean plays a critical role in determining the spatial distribution of atmospheric carbon dioxide. However, there is still a great deal of uncertainty in both magnitude and regional patterns of anthropogenic uptake associated with estimates of oceanic carbon fluxes. Using a recently developed technique, exchange of anthropogenic carbon dioxide across the air-sea interface have been estimated from observations of dissolved inorganic carbon and nutrient concentrations and an Ocean General Circulation Model (OGCM) using a Green's function inverse modeling technique. Previous sensitivity studies have shown that model circulation error is an important source of error in the ocean inversion. In order to address the role of ocean circulation biases, inverse estimates of anthropogenic carbon air-sea gas exchange are presented using basis functions from a suite of seven different OGCM's. The robustness of the ocean inversion will be quantified and the effects of differences between approaches to modeling ocean circulation on the ocean carbon cycle will be explored. These results will be discussed in the context of recent atmospheric inverse estimates.

URL: http://quercus.igpp.ucla.edu/OceanInversion

A31H-02 1200h

The Atmospheric Signatures of Terrestrial Ecosystem Processes: Results From a Coupled Atmosphere-Ecosystem Model

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Global-scale analyses of weekly CO_2 flask samples have shown that a number of terrestrial regions are significantly affecting the rate at which carbon dioxide is building up in the atmosphere. However, the observations used in these studies come primarily from stations that sample the marine boundary layer in order to eliminate variance due to terrestrial fluxes, making it difficult to identify the processes responsible for the observed patterns of terrestrial CO_2 flux. To address this issue, we have developed a regional-scale, coupled atmosphere-ecosystem model capable of assimilating observations from a diverse array of data sources, including eddy-flux measurements of surface CO_2 fluxes, measurements of atmospheric CO_2 concentrations obtained from aircraft and tall towers, and observations of canopy structure and dynamics obtained from satellite observations and forest inventory data. The model consists of a newly-developed, mass-conserving version of the mesoscale Regional Atmospheric Modeling System model (RAMS) coupled to the Ecosystem Demography Model (ED), which is able to represent the influence of both long-term and short-term processes on patterns of terrestrial CO_2 flux. We are using the coupled RAMS-ED model to perform forward and inverse modeling studies of regional carbon budgets within the North American continent. Preliminary results highlight the model's ability to connect regional patterns of atmospheric CO_2 to the underlying state of the ecosystems within a region.

A32A MCC: Level 1 Wednesday 1330h

Biogenic Reactive Trace Compounds and Their Role in Atmospheric Chemistry and Climate IV Posters

(joint with B, OS)

Presiding: **I Faloona,** University of California, Davis**; J Kesselmeier,** Max-Planck-Institute-Mainz

A32A-0105 1330h POSTER

Simulation of BVOC Fluxes and Chemical Transformations with a One-dimensional Canopy Chemistry Model for the BEWA Campaigns

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Numerical modeling can help to investigate the role of the different pathways for chemical degradation of biogenic volatile organic compunds (BVOC) and the effect of chemical reactions on the net BVOC fluxes from forest canopies. Starting from specified initial conditions the one-dimensional canopy-chemistry model CACHE predicts profiles of temperature, humidity, and chemical species. CACHE includes the energy balance at the leaf surfaces, vertical turbulent transport of heat, water vapor, and gas phase chemical compounds within and above the canopy, emission of biogenic VOC, chemical transformation and deposition of chemical constituents, and heat and moisture transport in the soil. Simulations with CACHE were carried out as part of the joint project BEWA 2000 for the 22 'golden days' during the summer 2001 and 2002 field campaigns at the Waldstein site (Fichtelgebirge, Germany). For the measuring site - a 20 m high spruce forest - the observed diurnal course of temperature and ozone are reproduced well by the model. Nighttime deposition was found to have a major effect on the diurnal course of the ozone concentration. A comparison with the REA measurements during the BEWA campaigns shows that the monoterpene fluxes and concentrations are generally reproduced very well. Furthermore, the fluxes of photooxidants like H_2O_2 show good agreement between measured and modeled values. The simulations however indicate, that it is necessary to include the emission of aldehydes and acetone in order to reproduce the observed fluxes and concentrations of these species. The model results show that during the daytime the effective fluxes at the canopy top are generally about 10 % lower than the potential fluxes, i.e. the fluxes without considering chemical degradation within the canopy. It was found that even during daytime the NO_3 radical can contribute significantly to monoterpene degradation in the lower part of the canopy. For example, within the canopy NO_3 contributes 30 to 50 % to the total degradation of limonene at noontime.

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

A32A-0106 1330h POSTER

Elements of a Process-based Model of Leaf Photosynthesis

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Process-based modelling of photosynthesis requires appropriate description of leaf photosynthesis. Essential aspects are stomatal conductance and the CO_2 assimilation proper, both as affected by the environment.

Here we propose and analyse a photosynthesis model with two variables (stomatal conductance (g_s) and the CO_2 partial pressure inside the leaf (p_i)) for the stomatal part and five variables to model the Calvin cycle intermediates. The actual stomatal conductance is calculated via a target function $G(I, \Delta VP)$ which describes the effects of light (I) and vapour pressure deficit (ΔVP). CO_2 fixation is modelled as a sink term for p_i so that a differential equation for p_i is derived which greatly simplifies explicit modelling of the Calvin cycle. A plausibility check of the model employing sinusoidal time courses for I and ΔVP is carried out. Using field data, the model is shown to produced a reasonable fit to data sets collected for oak leaves. Preliminary modelling results indicate that also the Calvin cycle intermediates and ATP are in acceptable agreement with experimental data. The model is intended to use as a base module of the isoprene emission model (SIM-BIM), which is a subproject of the BEWA2000 project within the national joint research project AFO2000 (Atmosphaeren Forschungsprogramm 2000).

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

A32A-0107 1330h POSTER

Observations on the Exchange of Oxygenated Compounds and Isoprenoids Between Tropical Tree Species and the Atmosphere During Different Seasons and Developmental Stages

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The terrestrial vegetation is the dominant source (>80%) for atmospheric volatile organic compounds (VOCs) on a global scale. These trace gases (i) influence the production or atmospheric lifetimes of air pollutants and greenhouse gases such as ozone, carbon monoxide, and methane, (ii) are involved in aerosol particle growth and production and (iii) contribute to the carbon budget of plants and ecosystems. Seasonal events may have significant impact on the exchange of VOCs between vegetation and the atmosphere. We report about the contrasting behaviour of tropical floodplain species in comparison to terra firma trees and the differences of emission quality and quantity of tree species during the wet and dry season in Amazonia. VOC emission changes in terms of quality (for example isoprenoid composition) or quantity (emission factors) and should be considered for an accurate estimation of the annual VOC release from tropical vegetation. Furthermore results from measurements on a deciduous Amazonian tree species demonstrate pronounced variations in the VOC exchange pattern depending on the developmental stage of the leaves.

A32A-0108 1330h POSTER

Micrometeorological Influences on Mass Transfer of BVOC?s at the Canopy Atmosphere Interface

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The interactions between micrometeorological, plant physiological, hydrobiological and chemical processes on the net gas fluxes of BVOC's into the atmosphere on the stand scale from different field experiments (ECHO 2002, 2003; BEMA 1993-1997) are analyzed. Terms of the balance equations for micrometeorological and scalar quantities up to the third moment are determined from measurements. The influences of advection, convection and turbulence and the role of hydrological conditions on mass budgets will be discussed. In addition, the influence of the water status on mixing time scales and chemical reaction time scales will be analyzed.

A32A-0109 1330h POSTER

Relationships Among Canopy Scale Energy Fluxes and Isoprene Flux Using Eddy Covariance Measurements Over Multiple Growing Seasons

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Isoprene is one of the most abundant biogenic trace gases in the troposphere. Biogenic trace gases affect tropospheric chemistry by forming gaseous and particulate secondary products in conjunction with anthropogenic emissions that contribute to the degradation of air quality. Our understanding of the impact isoprene has on tropospheric photochemistry is hampered by our limited knowledge of the biosphere-atmosphere exchange process, and thus the inability to accurately quantify the biogenic emission inventory. Isoprene emissions are regulated by many environmental variables; the most important variables are known to be temperature and light. The research summarized here seeks to improve our understanding of biogenic emissions from forest ecosystems as a basis for advancing our ability to describe the role of biogenics in regional and global atmospheric chemical cycles. Biogenic emission models, such as BEIS (Biogenic Emission Inventory System) rely on above canopy environmental parameters and below canopy scaling factors to estimate canopy scale biogenic hydrocarbon fluxes. This type of model can predict biogenic emissions well, however, the required input is extensive, and for regional applications, it can be cumbersome. Based on the assumption that isoprene emission rates are enzymatic (a function of temperature, light, and historical temperature), we propose that sensible heat flux can be a surrogate for above canopy temperature and light when estimating isoprene fluxes at the canopy scale. In addition, sensible heat flux may be a better indicator of the canopy interaction with incoming energy, as opposed to scaling above canopy parameters. Thus, the use of surface energy fluxes such as sensible heat flux is an attempt to combine the biological (enzymatic) and meteorological processes that affect the biosphere-atmosphere exchange of isoprene. Since surface energy budgets are an integral part of mesoscale meteorological models, this could potentially be a useful tool for including biogenic emissions into regional atmospheric models. Long-term measurements of isoprene flux have been collected above a northern hardwood forest at the AmeriFlux site located at the University of Michigan Biological Station (UMBS) as part of the Program for Research on Oxidants: Photochemistry, Emissions, and Transport (PROPHET). Measurements have been made every summer since 1998 using eddy covariance techniques, and the data are now available for determining the relationship between isoprene flux and surface energy fluxes. Using this long-term dataset we hope to improve our understanding of isoprene emissions and, thus, improve our ability to include isoprene emissions in regional and global atmospheric chemistry models.

A32A-0110 1330h POSTER

Investigation of Gas Phase Oxidation of Isoprene by OH Radicals in the Atmosphere Simulation Chamber SAPHIR

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Large emission rates from the biosphere and very high reactivity towards OH make isoprene particularly important in local and regional air chemistry. Concurrent measurements of isoprene and its primary oxidation products methyl vinyl ketone (MVK) and methacrolein (MACR) during the 2002 field campaign ECHO in Juelich, Germany, showed concentration ratios of MVK to MACR which could not be reproduced with current atmospheric reaction (box) models. We used the atmosphere simulation chamber SAPHIR at the Research Center Juelich to investigate the OH radical induced isoprene oxidation under nearly the same atmospheric conditions as they were encountered during the field campaign. Simultaneous measurements of isoprene, MVK, MACR, OH, HO_2, O_3, HCHO, NO, NO_2, and the photolysis frequencies of NO_2, O_3, and HCHO were used to constrain the model calculations. A photochemical model using a recently published updated degradation scheme for isoprene was applied to design and interpret the simulation chamber experiments. This new isoprene module is implemented into the Regional Atmospheric Chemistry Mechanism, RACM. We further upgraded this mechanism to explicitly treat the stable oxidation products MVK and MACR as individual species. The model analysis of the chamber experiments showed for the first time that the formation yields of MVK and MACR and therefore their ratio is strongly dependent on the NOx concentration due to the competition between the self-reaction of the primarily formed isoprene peroxy radicals and their reaction with NO. For very low NOx the ratio MVK/MACR is around 0.6 and rapidly increases to 1.5 for NOx above 100 ppt. We found a 30% higher yield of methacrolein compared to the literature (MCM V3), the yield of methyl vinyl ketone was confirmed. The rate coefficients of MVK and MACR with OH were found to be 20% lower as known so far (Atkinson 1986).

A32A-0111 1330h POSTER

Methanol and Acetone Fluxes from Agricultural Soil During the Summer 2003 European Heat Wave

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Field measurements of volatile organic compound (VOC) fluxes have often been carried out using enclosure measurements on single branches or young whole plants. Micrometeorological methods have been restricted to the flux gradient method or, more recently, to the relaxed eddy accumulation (REA) method, because fast response VOC sensors have not been available. In addition, most VOC flux measurements have been carried out above forested regions, while little is known about the VOC flux characteristics of savannas, grasslands, pastures, and grain production. We used the novel Proton-Transfer-Reaction Mass Spectrometer (PTRMS) as a fast VOC sensor to measure methanol and acetone mixing ratios used for eddy covariance analysis to yield methanol and acetone fluxes above an agricultural field prior to seeding. The field site belongs to the German federal agricultural research station (FAL), Braunschweig, and is 81 m a.s.l. Annual mean temperature at the site is 8.8° C with an average precipitation of 618 mm. The soil type is cambisol / loamy sand (pH 6.5; organic matter content 1.4 %). First measurements were carried out during the European heat wave in August 2003. Daytime air temperatures between August 8 and 13 reached up to 40° C and rarely fell below 20° C at night. Sensible heat flux exceeded 300 W m^{-2} at times. Both methanol and acetone were measured at 4 Hz for 30 min on an alternating half-hour schedule. Mixing ratios (up to 35 ppb for methanol and 10 ppb for acetone) showed diurnal variation with higher values during low turbulence times, especially at night, clearly indicating regional sources. Fluxes were always positive and reached up to 0.35 mg C m^{-2} h^{-1} for methanol and 0.1 mg C m^{-2} h^{-1} for acetone. Methanol fluxes showed a typical temperature dependence with a β-factor around 0.1, while acetone fluxes did not. Though the highest methanol fluxes occurred during the highest sub-soil temperatures, a significant correlation to the soil temperature at either five or ten centimeters depth was not found. Rather, the highest flux preceded the highest air temperature by approximately two hours, indicating that topsoil temperatures, measured to exceed 50° C at times, were the major driver of methanol fluxes.

A32A-0112 1330h POSTER

Aqueous Reaction of Methanol and Nitric Acid: Formation of Methyl Nitrate via Aerosol Chemistry

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Biogenic emissions of methanol are estimated to provide more than 75% of the global sources of this oxygenated VOC, and oceanic (possibly biological) contributions have also been postulated. Methanol has an atmospheric lifetime on the order of 10 days, allowing it to reach the upper troposphere. It is soluble in water and acidic solutions, which make up the

majority of particles in this region. Thus, the chemical behavior of methanol in aerosol particles and cloud droplets warrants consideration. As a first step in our laboratory investigation of the atmospheric multiphase chemistry of methanol, we will present spectroscopic evidence for reaction between methanol and nitric acid in aqueous sulfate solutions. Under acidic conditions, methyl nitrate is released, suggesting that some fraction of NOx may be liberated from nitric acid before it is removed from the atmosphere by wet deposition. Preliminary temperature-dependent studies suggest a significant reduction in rate as the temperature is reduced from 20°C to 10°C. Data for solutions of varying composition will be presented to allow evaluation of this reactive pathway over a variety of tropospheric conditions. Implications for methyl nitrate formation and HNO_3-to-NOx recycling will also be discussed.

A32A-0113 1330h POSTER

A Measurement of Gaseous and Particulate Biogenic Semi-Volatile Organic Compounds in the Forest Atmosphere with an Annular Denuder Sampling System

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Atmospheric concentrations of biogenic semi-volatile organic compounds (SOCs) in both gas and particle phase have been measured in two experimental forests with an annular denuder sampling system. The sampling sites were an experimental forest of Hokkaido University at Moshiri in Hokkaido Island, northern Japan (from August 22 to 29, 2002) and an experimental forest of Duke University at Chapel Hill in North Carolina, east coast of the United States (from July 9 to 12, 2003). The compounds detected in the forest atmosphere are glycolaldehyde, hydroxyacetone, n-nonanal, n-decanal, glyoxal, methylglyoxal and 4-oxopental. Glycolaldehyde, hydroxyacetone and methylglyoxal are known as oxidation products of isoprene which has the largest emission rate of any hydrocarbon species. Nonanal and decanal are probably directly emitted from vegetation. 4-oxopentanal is an oxidation product of 6-methyl-5-hepten-2-one. This is an oxidation product of organic compounds which are abundant on plant surfaces. All of these compounds were detected in both gas and particle phases. Their concentrations ranged from the detection limit (approximately 1 pptv) to 154 pptv (630 ng m-3, 4-oxopentanal), and the particulate concentrations ranged from the detection limit (approximately 3 ng m-3) to 200 ng m-3 (4-oxopentanal) in Moshiri, 2002. The gaseous concentrations of these compounds showed a clear diurnal variation on fine days. Although their production processes are different each other, the variation showed the same pattern which was quite similar to the ambient temperature. On the other hand, partition ratios (particle/(gas+particle)) of these compounds suggested that the process of gas-to-particle conversion of these SOCs is different between water soluble compounds and insoluble compounds. The partition ratios of water soluble compounds such as glycolaldehyde, hydroxyacetone and 4-oxopentanal (their Henry's constant exceed 10000 mol kg-1 atm-1) depends on relative humidity at the sampling site. This result suggested that water soluble SOCs can convert into particles via dissolution into aerosols existing in the atmosphere, and this is a particular process for the soluble SOCs. In this presentation, we will compare the emission and removal processes of biogenic SOCs in the forest atmosphere of Northern Japan with those in the East Coast of the United States. The observed SOCs behavior at the Duke Forest site is compared with VOCs and aerosol chemical composition observed by other investigators during the CELTIC study.

A32A-0114 1330h POSTER

Eddy Covariance Fluxes of Peroxyacetyl Nitrate (PAN) to a Coniferous Forest

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As part of the CELTIC study, we have used a fast response chemical ionization mass spectrometer (CIMS) system to make rapid measurements (4 Hz) of peroxyacetyl nitrate (PAN). Concurrent fast wind velocities were then used to obtain direct eddy covariance fluxes of PAN. Fluxes were measured for eight consecutive days in July, 2003 at a loblolly pine forest in North Carolina. Covariances between PAN concentration and vertical wind velocity indicated consistent deposition fluxes that ranged up to approximately -12 ngN m^{-2} s^{-1}. The average daytime flux was $\sim$ -2.5 ngN m^{-2} s^{-1} and the diurnal profile was consistent with uptake through plant stomates. Deposition velocities also showed a daytime maximum with an average daytime value of 7.1 mm s^{-1}. There was also some indication of nocturnal uptake when canopy elements were wet. These preliminary measurements suggest that uptake of PAN to forest canopies is significant and may play a role in both atmospheric chemical processes and nitrogen cycling within ecosystems.

A32A-0115 1330h POSTER

Virtual Disjunct Eddy Covariance Flux Measurements of Biogenic Volatile Organic Compounds from Ponderosa and Loblolly Pine Forests using Proton Transfer Reaction Mass Spectrometry

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Biogenic emissions of trace organic compounds into the atmosphere impact the levels of oxidants such as ozone and hydroxyl radicals and effects secondary organic aerosol formation. In an attempt to quantify these emissions, we used the virtual disjunct eddy covariance method and a Proton Transfer Reaction Mass Spectrometer (PTR-MS) during two summer 2003 field campaigns to measure the flux of several biogenic volatile organic compounds (VOCs). The first campaign was part of the CELTIC study in a North Carolina Loblolly pine plantation (Duke Forest) designed to study Chemical Emission, Loss, Transformation, and Interactions within Canopies. The second campaign was at the Black Hills Ameriflux Tower near Rapid City, South Dakota. Significant fluxes of acetaldehyde, isoprene, acetone, methanol, methylbutenol, and monoterpenes were measured and a comparison between isoprene flux measurements from the PTR-MS and a Fast Isoprene System was performed. Compound identities were verified using gas chromatography with a PTR-MS as the detector.

URL: http://acd.ucar.edu/~cstroud/CELTIC/

A32A-0116 1330h POSTER

Above Canopy Emissions of Isoprene and Monoterpenes from a Southeast Asian Tropical Forest

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Fluxes of isoprene were measured using the eddy covariance technique and an ozone chemiluminescence isoprene sensor above a secondary tropical forest/rubber tree plantation located in the Xishuangbanna region of southern China during the wet and dry seasons. Fluxes of monoterpenes were inferred from ambient boundary layer concentrations (wet season) and from relaxed eddy accumulation measurements (dry season). Isoprene emissions were comparable to what has been observed from other tropical forests in Africa and South America. In this forest, monoterpene emissions were much higher during the wet season due to the senescence of the rubber trees during the dry season. These flux measurements represent the first ecosystem level flux measurements reported from Southeast Asian tropical forests.

A32A-0117 1330h POSTER

Eddy Correlation Measurements of the Air/Sea Flux of DMS Using Atmospheric Pressure Chemical Ionization Mass Spectrometry

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The physical and chemical processes controlling gas exchange across the air/sea interface are not well understood. Many laboratory and field studies of the physical controls on gas exchange have been performed using indirect mass balance measurement techniques, but there have been few direct gas flux measurements over the ocean. Eddy correlation is a micrometeorological technique, which can measure fluxes directly. The use of this technique for trace gas flux measurements has been limited in part due to the lack of sufficiently sensitive, fast-response gas detectors. Atmospheric pressure chemical ionization mass spectrometry (API/CIMS) is a highly sensitive, fast response detection method. We carried out a field study at the Scripps Institute of Oceanography pier to test the use of API/CIMS for eddy correlation flux measurements of dimethylsulfide (DMS). Cospectra of vertical winds and DMS demonstrate that flux from the sea surface was routinely detected. The API/CIMS detected atmospheric fluctuations less than 0.5 Hz. This frequency cut-off probably reflects attenuation in the inlet tubing rather than in the detector itself. The partial pressure of DMS in surface seawater was also determined using the API/CIMS, after equilibration with N2 in a continuous flow membrane equilibrator. Gas exchange coefficients were computed from the flux and air/sea concentration gradient. Gas transfer coefficients determined in this study ranged from 0.66 cm/hr to 38.43 cm/hr, for mean horizontal wind speeds ranging from 1 to 6 m/s. The gas transfer coefficients are positively correlated with wind speed, but are significantly greater than current estimates of gas transfer coefficients at similar wind speeds over the ocean. These elevated gas transfer coefficients probably reflect enhanced waterside turbulence induced by the interaction of wave motion with the shallow bottom at this site.

A32A-0118 1330h POSTER

Measurement of trace gas emissions of spruce (Picea abies) by different techniques including PTR-MS at the BEWA field campaign 2002

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Proton transfer reaction mass spectrometry (PTR-MS) was used to measure VOC fluxes from Norway

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spruce (Picea abies) during the BEWA field campaign 2002. The BEWA measuring tower is located in the Bavarian "Fichtelgebirge" at 50°09' N and 11°52' E in Germany. The site is at 776 m a.s.l. and has got an alpine-like climate. A dynamically flushed enclosure system was used for the measurement of trace gas emissions: One enclosure was kept empty as a reference. The other enclosure contained a spruce twig of ca. 8 cm length at a height of about 13 m from the ground. The main compounds monitored on-line were methanol, acetaldehyde, acetone, isoprene, and the monoterpenes. The PTR-MS system continuously analysed all selected VOCs in the air from the plant enclosure over a 3 minute cycle. The empty enclosure was measured every hour. From these data emission rates were calculated. By the use of different algorithms standard emission rates for all compounds were determined. The results for isoprene and monterpenes lie within the values reported in the literature, however on the lower limit. Apparently plants had adapted to the low temperatures during the field campaign. Carbonyl compounds were also determined by DNPH-cartridges and subsequent HPLC-analysis. A comparison of DNPH and PTR-MS results will be given.

A32A-0119 1330h POSTER

Quantification of carbon sources for isoprene emission in poplar leaves

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Isoprene is the most abundant volatile organic compound emitted by plants and in particular by trees. Current interest in understanding its biosynthesis in chloroplasts is forced by the important role isoprene plays in atmospheric chemistry. Leaf isoprene formation is closely linked to photosynthesis by a dynamic use of recently fixed photosynthetic precursors in the chloroplast. Under steady state conditions in [13C]CO2 atmosphere approximately 75 % of isoprene became labeled within minutes. The source of unlabeled C is suggested to be of extra-chloroplastidic and/or from starch degradation. In order to test whether these alternative carbon sources - leaf internal C-pools and xylem-transported carbohydrates, contribute to leaf isoprene formation in poplar (Populus tremula x P. alba) on-line proton-transfer-reaction-mass spectrometry (PTR-MS) was used to follow 13C-labeling kinetics.

A32A-0120 1330h POSTER

Terpene Emissions From a Deciduous Forest - Variation of Compound Composition and Emission Rates

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Plants emit a complex mixture of volatile organic compounds (VOCs). These hydrocarbons play an important role in atmospheric chemistry because of their high chemical reactivity. Due to the complexity of the chemical system there are still large uncertainties about environmental and especially physiological influences affecting amount and pattern of these emissions. In general, VOC emissions are affected by meteorological parameters like temperature and light intensity as well as ecophysiological parameters like herbivore attack and allelopathic effects. Moreover an influence of the developmental status of the emitting plants is likely. Aim of our work was to get insight in the emission behaviour concerning terpenes by carrying out long-term measurements in the field. Applying the branch enclosure technique terpene emissions from beech (Fagus silvatica L.) were investigated for two successive vegetation periods (2002-2003). In both years main compounds emitted were the monoterpenes sabinene, alpha- and beta-pinene and tricyclene. The emission rates changed over the day up to two orders of magnitude as a function of temperature and light. While the specific emission patterns changed only little over the year, the emission rates showed significant variations. Highest emission rates were observed in summer and lowest were found in fall. However, no emissions were found in early spring although leaves were fully developed and temperature and light conditions were moderate. Moreover a seasonality characterized by a temperature independent decline of emissions in late summer was found. The results underline the importance to characterize the annual variation of emission behavior. Especially for the up-scaling to global VOC emissions, seasonal influences have to be considered to achieve realistic emission inventories.

A32A-0121 1330h POSTER

Precipitation controls isoprene emissions from tropical ecosystems

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Isoprene emissions from tropical regions account for a majority of isoprene produced globally. Current estimates of global isoprene emissions use meteorological inputs (temperature and light), ecosystem leaf area, and a time invariant, ecosystem specific emissions factor. This approach has been verified to work well for deciduous mid-latitude forests, but the approach has not been tested for tropical ecosystems where seasonality is induced by precipitation. Recent flux studies at two field stations in the tropics found strong effects of precipitation regime (dry vs. wet season) on isoprene emissions. A flux study conducted during the wet season (October 1999) at the La Selva Biological Station (10° 26′ N, 83° 59′ W, precipitation 4000 mm yr^{-1}) found whole system isoprene emissions rates between 2–10 mg C m^{-2} h^{-1}, while a second campaign during the dry season (April 2003) found values ranging 8–16 mg C m^{-2} h^{-1}. This difference could not be explained by changes in ambient temperature or light using established emissions algorithms. The second field site near Santarém, Brazil in the Floresta Nacional do Tapajós (2° 51′ S, 54° 58′ W, precipitation 2000 mm yr^{-1}), part of the Large scale Biosphere-atmosphere experiment in Amazônia (LBA), showed a similar pattern. Additionally, a 13 month isoprene concentration record at this station found a 4 fold increase during the dry season. Application of a one dimensional chemistry model predicts a similar change in isoprene source strength. A standard emission model using temperature and light could not account for these seasonal changes, but adding an empirical term that accounted for previous precipitation greatly enhanced the fit.

A32A-0122 1330h POSTER

Investigations on stomatal uptake of carbonyl sulfide (COS, OCS) and deposition velocities result in new estimates of global COS deposition to vegetation.

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Carbonyl sulfide (COS, OCS) is a highly stable reduced sulfur gas species in the atmosphere. Due to its inertness within the troposphere it can be transported into the stratosphere where it contributes to form SO2 and sulfate aerosol. Additionally it may be involved in heterogeneous reactions in stratospheric ozone chemistry. One of the major sinks for this trace gas is the vegetation. Based on investigations with trees under a light and dark regime and reacting to the hormone abscisic acid we demonstrated the stomatal uptake of COS to be the dominating pathway for COS deposition to plant surfaces. Taking into account deposition velocities of COS, which are higher than for CO2, we recalculated the global COS deposition to vegetation based on a new refined estimation model.

A32A-0123 1330h POSTER

HO_x Radical Measurements During the ECHO Field Campaign in Summer 2003

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Atmospheric OH and HO_2 radical concentrations were measured during a field campaign in July 2003 in a forest in Juelich, Germany. The campaign was part of the ECHO project which investigates the emission and chemical processing of biogenic volatile organic compounds (VOC) in and above a mixed forest stand, in order to derive improved estimates of net emissions of biogenic compounds and their possible degradation products into the planetary boundary layer. The OH radicals, which can provide a major sink for VOCs, were detected directly by laser-induced fluorescence (LIF) at 308 nm. The HO_2 radicals, which can result from reactions of VOCs with radicals like OH or NO_3, were measured by LIF following the conversion of HO_2 into OH by reaction with NO. During the campaign, a newly developed LIF instrument was deployed which is much more compact and light weighted than the instrument previously used by our group. The relatively small size of the new instrument (foot-print 150 x 70 cm) allowed to place the instrument on a movable platform that could be lifted up and down along a 38 m high tower which was set up in the forest. On the same tower, a comprehensive set of meteorological parameters and other trace gases (NO_3, O_3, NO_x, VOC, HCHO, HONO, PAN, photolysis frequencies etc.) was measured at different heights above ground. The experimental set up was successfully used a) to measure diurnal variations of radicals and trace gases in and above the canopy and at ground in the forest, b) to measure for the first time vertical concentration gradients of OH and HO_2 near ground up to 38 m altitude, and c) to detect fast variations of HO_x radical concentrations with an improved time resolution of 5.5 s. During the intensives of the campaign more than 6 diurnal cycles were measured and 14 vertical profiles at day and nighttime were achieved. This contribution presents the experimental set up of the radical measurements during the ECHO campaign and first results from our radical measurements.

A32A-0124 1330h POSTER

Footprint Experiments in a Model of a Complex Forest Stand (ECHO Site)

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This study takes part to the project "Emission and CHemical transformation of biogenic volatile Organic compounds: investigations in and above a mixed forest stand" (ECHO) funded by the German atmospheric

research program AFO 2000. The contribution of Hamburg University is a better understanding of the transport of biogenic emissions in the atmospheric boundary layer influenced by a very rough environment as a finite forest area. The finite forest area surrounding the Research Centre of Jülich (Germany) was modelled to a scale of 1:300 and studied in the large boundary layer wind tunnel of the Meteorological institute of Hamburg University. The model of the forest must reproduce the resistance to the wind generated by this porous environment. Using rings of metallic mesh to represent some group of trees, some preliminary tests were carried out to find the arrangement of these rings that would provide the appropriate aerodynamic characteristics for a forest. The agreement between wind and turbulence profiles measured in the wind tunnel and in the field ensured that the physical modelling of the complex forest area was realistic. The comparison of the turbulence properties of the flow, inside and above the canopy, with the literature about dense canopies showed strong similarities for the spectral densities and integral length scale profiles. Since the flow structure inside the forest area is well replicated, further measurements can be carried out on the model of the complex forest stand in order to answer questions of project partners. During field campaigns in the ECHO site, profiles of VOC concentrations are measured at three different measurement towers located in the forest stand. The origin, the trajectory and the travel time of these biogenic emissions are very important parameters for the analysis of the field data. In consequence, footprint experiments were performed in the wind tunnel by moving a release point source all over the forest area upwind of the measurement towers, and measuring which fraction of tracer-gas reached the measurement towers. These experiments gave the distribution of the probability of origin of the emissions, which are sampled at the measurement towers. The principal outcome was that the inhomogeneity of the forest (clearings and the presence of the research center within the forest) plays a disturbing role in the dispersion process of the emissions. Air masses with completely different trajectories and histories are simultaneously sampled, mixed and analyzed during field experiments. The few clearings located in the forest cause the upward deflection of air masses, which were in contact with the ground. In consequence, the contribution of biogenic emissions from the soil must not be neglected, even in the analysis of samples taken above the canopy. Some simple relationships to quickly estimate the travel time and the travel height of the air masses inside this specific forest, just knowing the wind speed at the monitoring station, were also proposed. In a next future, the vertical transport of the emissions above the forest will be studied in the physical model of this complex forest area. In order to replicate in the model the emissions released by the trees, an area source releasing gas at 80% of the tree height (location of the tree crown) will be designed and the turbulent mass fluxes above the canopy will be measured.

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

A32A-0125 1330h POSTER

Atlantic Ocean Measurements of Low Molecular Weight Alkyl Nitrates

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The surface oceans appear to be a source of low molecular weight alkyl nitrates to the atmosphere. These compounds are converted by photolysis to NOx, and may contribute to ozone production in remote regions. The mechanism(s) of production of oceanic alkyl nitrates in surface seawater are currently unknown. Laboratory studies suggest that the reaction of peroxy radicals with nitric oxide in seawater may provide a near-surface source of these compounds. These precursors originate from the photolysis of dissolved organic matter and nitrite. Depth profiles of alkyl nitrates in the North Atlantic Ocean (Chuck et al. 2002) show elevated concentrations of alkyl nitrates below the photic zone, suggesting that non-photochemical mechanisms are also likely. We have recently completed a series of alkyl nitrate (C1-C3) depth profiles and shipboard incubation experiments in the north Atlantic, on a cruise track from Reykjavik, Iceland to Natal, Brazil (A16N2003; R/V Brown). The northernmost stations (45-50N), exhibited alkyl nitrate maxima in the mixed layer, and a positive correlation between alkyl nitrates and nitrite. In the tropics and subtropics, alkyl nitrate maxima were below the mixed layer, and alkyl nitrates correlated with nitrate. Shipboard deck irradiation studies demonstrated photochemical production of alkyl nitrates in waters that correlated with the initial nitrite concentration. Addition of nitrite stimulated production to extremely high levels, suggesting that NO, rather than peroxy radicals, is the limiting reactant in these waters. Overall, the distribution of alkyl nitrates suggests that both photochemical and microbial sources of alkyl nitrate may occur.

A32A-0126 1330h POSTER

A Biogenic Role in Exposure to Two Toxic Compounds.

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Biogenic sources play an important role in ozone and particulate concentrations through emissions of volatile organic compounds. The same emissions also contribute to chronic exposures to toxic compounds such as formaldehyde and acetaldehyde. Anthropogenic sources may dominate over biogenic sources in both primary and secondary production of both compounds. However, modeling tools are becoming able to answer how biogenic and anthropogenic sources contribute to both processes. Biogenic emissions models can predict formaldehyde and acetaldehyde emissions. Photochemical models can isolate how biogenic emissions contribute to the primary and secondary components of formaldehyde and acetaldehyde concentrations. Initial modeling shows that biogenic versus anthropogenic contributions depend on the pollutant and location. For example in the primary component, anthropogenic sources determine formaldehyde concentrations over most locations but acetaldehyde has a large contribution from biogenic sources over rural locations. For the secondary component, both pollutants have a significant contribution from biogenic sources outside urban areas. This presentation discusses these contributions and their evaluation based on a model system called CMAQ. This work has been funded wholly by the United States Environmental Protection Agency. It has been subjected to Agency review and approved for publication.

A32A-0127 1330h POSTER

Atmospheric Behavior of Inorganic Water-Soluble Gas and Aerosol Species at a Rural Site in the Amazon Basin

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We investigated diel and seasonal variations of ammonia (NH_3), nitric acid (HNO_3), nitrous acid (HONO), hydrochloric acid (HCl) and the water-soluble inorganic aerosol species, ammonium (NH_4^+), nitrate (NO_3^-), nitrite (NO_2^-), chloride (Cl^-) and sulfate (SO_4^{2-}) on a pasture site in the Amazon Basin (Rondônia, Brazil) from September to November 2002 (LBA-SMOCC). Measurements were performed on-line using a wet-annular denuder in combination with a Steam-Jet Aerosol Collector (SJAC) supported by monitoring of meteorological quantities (e.g., relative humidity, air temperature, wind speed). Widespread biomass burning resulted in a significant enhancement of soluble trace gas levels, of which ammonia showed the highest abundance. We found a strong dependence of ammonia, nitric acid, and aerosol ammonium nitrate on meteorological parameters (especially air temperature and relative humidity) as well as on boundary layer conditions during day and nighttime. Deposition of soluble gases on wet surfaces at night was promoted by the increase of relative humidity to nearly 100 %. Obviously, re-evaporation of ammonia and nitric acid contributed effectively to increased mixing ratios in the turbulent boundary layer at daytime. Additionally, our measurements support the assumption of a continuous HONO source since a complete depletion at daytime was not found. Under clean conditions (wet season), HONO photolysis at daytime was very low and it is expected that its contribution to OH radical production was most likely small compared to the dry season (biomass burning). Our results provide important information about gas-aerosol interactions in a tropical region and the influence of meteorological parameters on emission and deposition processes of inorganic water-soluble species under biomass burning and clean conditions.

A32A-0128 1330h POSTER

Application of the Membrane Tube Technique for Simultaneous Measurements of Soil Air Concentration Profiles of NO, N_2O, CO_2, CH_4, and ^{222}Rn in a Temperate Forest Soil

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Using the membrane tube technique (METT), soil air concentration profiles of NO, N_2O, CO_2, CH_4, and ^{222}Rn were continuously measured in a typical luvic stagnosol in a German mixed forest of oak and birch (Juelich, Germany; 50° 54 N, 6° 24 E) during the ECHO field campaign in July 2003 (**E**mission and **CH**emical **T**ransformation of Biogenic Volatile **O**rganic Compounds). In April 2002 semipermeable tubes were installed at the soil surface and in 2, 7 and 12 cm depth. N_2O, CO_2, CH_4, and ^{222}Rn concentrations were measured with non-destructive methods in a closed cycle system to avoid soil air concentration changes by external gas input. Since NO was measured with a chemiluminescence technique ("destructive method"), the air sampled was replaced by air from a dilution system where the NO concentration was adjusted to the concentration measured in the soil. Soil air profile measurements were accompanied by simultaneous measurements of (a) profiles of soil moisture and soil temperature, (b) meteorological parameters, (c) soil chamber measurements (NO, NO_2, O_3, ^{222}Rn), and (d) physical and chemical soil parameters to put soil air concentration changes into context and to infer corresponding fluxes from the concentration profiles.

A32A-0129 1330h POSTER

Diurnal Variation of Non Methane Hydrocarbons and Carbon Monoxide in the Subantarctic Atmosphere

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Non methane hydrocarbons and carbon monoxide have been monitored during the El CID campaign in the Kerguelen Archipelago (49°21 S; 70°13 E) from January 22 to February 22, 2002. Non methane hydrocarbons were monitored in situ for the first time in these remote areas by using an automated GC. Over the whole period about 1400 measurements of C_2-C_5 NMHCs have been realized with a step time of 30 minutes. It was observed for the C_2-C_5 alkenes (in the range of 10 to 100 pptv) a very regular diurnal trend with mixing ratios systematically peaking at 15-16 H local time, i.e. shifted by about 3 hours off the solar noon. Simultaneously, the CO levels remained always comprised between 30 and 50 ppbv, i.e. a figure characteristic of pure marine air masses at these latitudes, but CO presented in the same way diurnal fluctuations of few ppbv strongly correlated with those of alkenes. On the opposite this diurnal trend was hardly visible for alkanes. The occurrence of a remarkable correlation between UV irradiance and alkene mixing ratios in the marine air supports the evidence of a photolytic production of alkenes by degradation of dissolved organic carbon (DOC) as pointed out by several other authors. Therefore from a 1D model, the budget of NMHC and CO in the atmospheric column was examined by considering the usual chemical processes of alkene destruction in the atmospheric column, and exchanges at the top of the boundary layer. Assuming that the magnitude of the marine source magnitude was dependent on the UV irradiance, the diurnal cycles observed were perfectly reproduced for alkenes as well as for CO. Based on simultaneous measurements of dissolved alkenes in seawater this marine source appears to be consistent

with strong alkenes (and probably CO) gradient within the seawater surface. Other synoptic observations including air masses back trajectories, and chlorophyll distribution in surface waters explain the variability of the alkenes and CO backgrounds consistent with the spatial variability of the marine photolytic source by degradation of DOC. Periods of high ventilation correspond also to significant changes in the alkanes/alkenes distribution in the atmosphere probably linked to turbulent mixing of surface water. Besides marine alkenes and CO similar features, our study finally support the existence of the measured significant levels (up to 100 pptv) of short lived NMHCs in the background subantarctic atmosphere due to their photolytic production by surface seawater; it also enables to conclude that different production mechanisms occur for alkanes involving possible biological processes in depth in the water column.

A32A-0130 1330h POSTER

NO emissions from arid ecosystems: first results from desert soils of Namibia

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Very recently it becomes evident, that arid and semi-arid soils may be a significant source of nitrogen oxide. As for most other soils, NO emission seems to be controlled by the availability of nitrogen containing nutrients and of soil water. Particularly, desert soils may provide rather high NO emissions just after seasonally limited and/or sporadical rain events due to the accumulation of nitrate and/or ammonium. We like to present some results of NO emission from desert soils which we have obtained through laboratory studies (and subsequent upscaling by a modified Galbally-Johansson algorithm) on soil samples from Namibia. Samples were taken in September/October 2001 between 18.55 - 24.43^{o}S, 15.02 -16.29^{o}E, and 464 - 1132 m a.s.l. We simultaneously determined NO production and NO consumption rates of the soil samples at different soil temperatures (25 and 35^{o}C) and for an appropriate range of soil moisture (dry to field capacity). NO production and consumption rates for dry soils are always close to the detection limit of our method (0.01 ng kg^{-1} s^{-1} and 10^{-5} m^{3} kg^{-1} s^{-1}, respectively), while wetting of the samples led to NO production rates up to 11 ng s^{-1} per kg of dry soil. We also determined soil nitrate and ammonium, as well as pH of the soil samples to put variation of rates and fluxes into context. Based on available climatological (soil temperature, rain) and soil chemical data, an attempt is made to estimate the contribution of Namibian desert soils to the regional budget of southern African emissions of NO_x.

A32A-0131 1330h POSTER

A Method for the Measurement of Nitrous Acid Flux Using Relaxed Eddy Accumulation

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HONO has recently received renewed attention as a byproduct of condensed nitrogen photolysis and as a potential atmospheric radical source. In particular, several recent accounts suggesting a photochemical source in forests have lead us to develop a method for assessing nitrous acid flux above a hardwood forest in northern Michigan. The technique was based on nitrous acid in ambient air being scrubbed into a 1mM phosphate buffer that was then derivatized into a light absorbing complex. A separate scrubbing system was used for updrafts and downdrafts after the air had been separated through Teflon valves according to input from a sonic anemometer. The detection of the complex was performed via UV absorption through a capillary flowthrough cell. Detection limit for this analytical method is around 10 pptv. Derivatized solution from each flow system was injected into the capillary cell via an 8-port valve with two sample loops. Each sample loop was injected as soon as it filled, which allowed measurement of all of the scrubbed material in each flow system. Laboratory tests were performed to assess the accuracy and suitability of this method. The field worthiness of the instrument was determined during the summer of 2003 at the University of Michigan Biological Station in northern Michigan where it was placed on top of a 35m tower above a forest canopy.

A32A-0132 1330h POSTER

Atmospheric Ammonia Emissions and a Nitrogen Mass Balance for a Dairy

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Atmospheric ammonia (NH_3) emissions have many impacts on the environment and human health. Environmental NH_3 impacts include terrestrial and aquatic eutrophication, soil acidification, and aerosol formation. Aerosols affect global radiative transfer and have been linked to human health effects. The global emissions of NH_3 are estimated to be 45 Tg N yr^{-1} (Dentener and Crutzen, 1994) with most of the emissions coming from domestic animals. The largest per animal emission come from dairy cows at 33 kg N animal-1 year-1 versus 10 kg N animal-1 -1 for cattle. On a global scale the emissions uncertainty is about 25%, but local emissions are highly uncertain (Bouwman et al., 1997). Local emissions determination is required for proper treatment in air pollution models. The main sources of emission from dairies are the cow stalls where urea and manure react to form NH_3, the storage lagoons where NH_3 is the end product of microbial degradation and the disposal of the waste. There have been numerous studies of NH_3 emissions in Europe but farming practices are quite different in Europe than in the U.S.. The impact of these differences on emissions is unknown. We have been studying the NH_3 emissions from the Washington State University dairy for three years to develop a detailed emission model for use in a regional air pollution model. NH_3 is measured using a short-path spectroscopic absorption near 200 nm with a sensitivity of a few ppbv and a time resolution of a few seconds. The open air short-path method is advantageous because it is self calibrating and avoids inlet wall adherence which is a major problem for most NH_3 measurement techniques. A SF_6 tracer technique has been used to measure fluxes from the three main emission sources: the cow stalls, anaerobic lagoon and the waste application to grass fields using a sprinkler system. Estimated yearly emissions from each source will be compared to a nitrogen mass balance model for the dairy.

A32A-0133 1330h POSTER

Identification and Quantification of Volatile Organic Compounds at a Dairy

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Livestock operations in the United States are an escalating environmental concern. The increasing density of livestock within a farm results in an increased emission of odorous gases, which have gained considerable attention by the public in recent years (National Research Council (NRC), 2002). Odorous compounds such as ammonia (NH3), volatile organic compounds (VOC's), and hydrogen sulfide (H2S) were reported to have a major effect on the quality of life of local residents living near livestock facilities (NRC, 2002). There has been little data collected related to identification and quantification of gaseous compounds collected from open stall dairy operations in the United States. The research to be presented identifies and quantifies VOCs produced from a dairy operation that contribute to odor and other air quality problems. Many different VOCs were identified in the air downwind of an open lactating cow stall area and near a waste lagoon at the Washington State University dairy using Gas Chromatography Mass Spectroscopy (GC-MS) analysis techniques. Identified compounds were very diverse and included many alcohols, aldehydes, amines, aromatics, esters, ethers, a fixed gas, halogenated hydrocarbons, hydrocarbons, ketones, other nitrogen containing compounds, sulfur containing compounds, and terpenes. The VOCs directly associated with cattle waste were dependent on ambient temperature, with the highest emissions produced during the summer months. Low to moderate wind speeds were ideal for VOC collection. Concentrations of quantified compounds were mostly below odor detection thresholds found in the literature, however the combined odor magnitude of the large number of compounds detected was most likely above any minimum detection threshold.

A32B MCC: Level 1 Wednesday 1330h

Chemistry and Dynamics of the Upper Troposphere and Lower Stratosphere III Posters *(joint with SA, AE)*

Presiding: **D Toohey,** Program in Atmospheric and Oceanic Sciences, University of Colorado**; E Richard,** NOAA Aeronomy Laboratory and CIRES

A32B-0134 1330h POSTER

Single Particle Measurements of the Chemical Composition of Cirrus Ice Residue

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The NOAA Aeronomy Laboratory's Particle Analysis by Laser Mass Spectrometry (PALMS) instrument is able to determine the chemical composition of the particulate matter found in the atmosphere. Individual particles are brought into a vacuum system where aerodynamic diameter is ascertained by the time required for passage between two visible laser beams. An excimer laser is then pulsed to hit each aerosol and desorb and ionize molecules and atoms. A complete positive or negative spectrum is provided by a time of flight mass spectrometer. The PALMS instrument was installed in the nose of a NASA WB-57F high altitude research aircraft throughout the 2002 CRYSTAL-FACE mission. PALMS was used in conjunction with a Counterflow Virtual Impactor (CVI) in order to separate ice crystals, which compose high altitude cirrus clouds, from the background aerosols which did not freeze. The ice crystals were subsequently melted and evaporated and the residual particles upon which they had formed were analyzed. The PALMS instrument was therefore able to determine what types of particles were responsible for the formation of the cirrus clouds encountered during CRYSTAL-FACE. The results will help elucidate the mechanisms responsible for ice formation in the atmosphere which are important to our understanding of the Earth's radiative budget.

URL: http://www.al.noaa.gov/PALMS/